

Impurity Effects in All-Vanadium Redox Flow Batteries

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Abstract

In this dissertation, the effects of VOSO_4 [vanadyl sulfate] source and impurities on the beginning-of-life (BOL) performance of an all-vanadium redox flow battery (VRFB) are explored. Battery performance was monitored at 50% state of charge (SOC) using electrolyte with VOSO_4 purities of 99%, 99.9% and 99.99% by weight. At cell potentials of 1.23V, the least pure solution yielded the lowest current density of 280 mA/cm^2 [square centimeter] and the most pure solution yielded the highest, 560 mA/cm^2 . The voltage efficiencies and charge-discharge capacities were shown to follow the same trends. Scanning electron microscopy (SEM) images revealed significant coverage of the electrode surface with deposited material, identified as Si. Blockage of electrode pores is proposed to be the primary reason for the BOL performance variation of the three suppliers tested. Filtration of low-purity electrolyte before testing was shown to remove the impurities, resulting in performance similar to high-purity electrolyte. Further testing explored the effects of adding 1% iron by weight in the form of ferric sulfate as an impurity.

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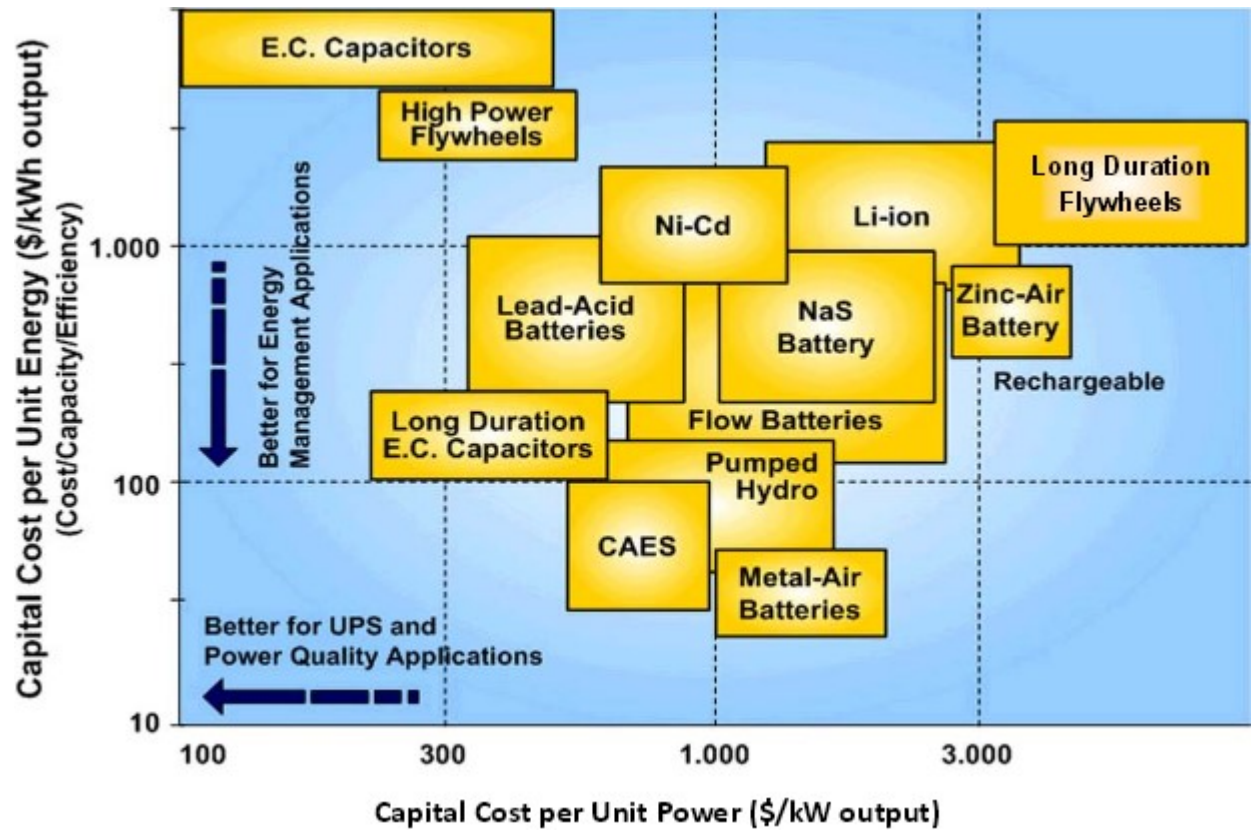
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Chapter 1: Introduction

The world produces a majority of its electricity from non-renewable sources, most prominently nuclear and fossil fuel [1]. By far the leading source of energy is fossil fuel, which comprises nearly two thirds of all energy production. As supply limitations of non-renewable energy sources come into view and climate change becomes a more pressing issue, global energy policy is gradually calling for implementation of renewables in the interests of national security, economic stability and energy independence. As the United States follows this trend by mandating a more diverse energy profile [2], the transient nature of most renewables becomes a more prominent hindrance to integrating them into the power grid. Intermittent energy production is particularly pernicious in wind and solar which happen to be the frontrunners of renewable research and implementation.

Without a national power infrastructure overhaul, the current power grid may become destabilized if renewables provide the power at the levels mandated. Grid destabilization can be avoided and new power infrastructure can be postponed with proper integration of energy storage. Energy storage is currently used in the United States, but the current national storage capacity is around 128,000 MW, which covers 12 % of US electricity generating capacity [3]. Over 99 % of energy storage currently implemented is derived from pumped hydro, which leaves significant opportunity for developing technologies. Redox flow batteries (RFBs) are a promising means of storing energy as they are a combination of good efficiency, relatively low capital cost, and low life cycle costs when compared to other technologies [4] as shown in Figure 1.

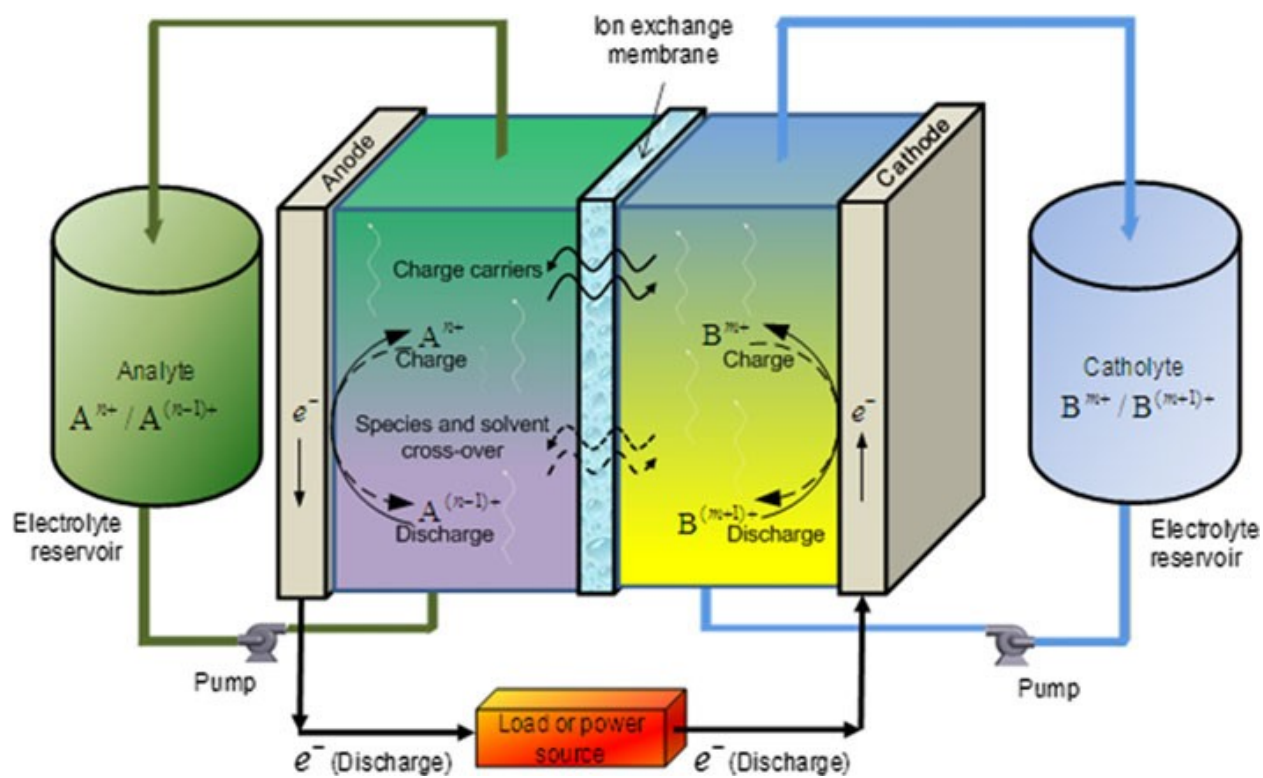
Similar to conventional batteries, flow batteries convert electricity into chemical energy via chemical reactions. Flow batteries are unique in that their power density and capacity are decoupled. Hybrid flow batteries also exist, but unlike true flow batteries, hybrids do not have decoupled power density and capacity because the metal being oxidized and reduced is plated in the stack. This means that increasing the battery capacity requires a larger stack. Since only true flow batteries have decoupled capacity and power generation, they are unique in that they enable modular installations of any desired capacity as long as enough space is provided. A redox flow



R. Carnegie, D. Gotham, D Nderitu, et. al., *Purdue State Utility Forecasting Group*, Jun. 2013.

Figure 1.1: Energy Storage Technologies

battery generates and stores energy using two redox couples. A redox couple refers to the two oxidation states that an active specie in a RFB changes between. Many redox couple pairs have been tested in RFBs, including iron/chromium, lithium/iodine, vanadium/bromine, iron/vanadium and all-vanadium. A couple is the storage mechanism behind a RFB is presented in Figure 2, which provides a visual for understanding how a redox flow battery works. Everything between the anode and the cathode is referred to as a cell which is where the electrochemical reactions take place which store electricity. The cell is comprised of two half-cells, positive and negative, where the active species change oxidation state. Catholyte and anolyte, which are more generally referred to as electrolytes, flow through either half-cell. The half-cells are separated by an ion-selective membrane which allows ions not associated with the redox reaction to pass through in order to balance charge changes from redox ions losing or gaining electrons. In practice, however, redox ions cross from one side to the other inducing losses. This is less of a problem with the all-vanadium chemistry because crossover losses can be recovered more effectively than other chemistries by mixing the positive and negative electrolyte together, dividing the solution between the two tanks, and recharging the electrolyte. Other chemistries suffer in this regard because remixing is harmful to performance. Because of the relatively high long-term viability of the all-vanadium chemistry, the research conducted has been focused on this chemistry. The primary problem with all-vanadium redox flow batteries (VRFBs) is that they are expensive. The estimated capital cost of VRFB systems is \$380/kWh [6], and a 30% reduction is needed to make them more commercially viable in the near future [7]. A direct way to mitigate cost is to use less expensive materials. The cost of the electrolyte, which accounts for 1/3 of capital costs [8], can be reduced by using lower purity reagents.



A. Z. Weber, M. M. Mench, J. P. Meyers, et. al., *J. Appl. Electrochem.*, vol. 41, pp. 1137–1164, Sep. 2011.

Figure 1.2: Redox flow battery diagram^[5]

Chapter 2: Literature Review

The effects of impurities have been well-studied in the field of polymer electrolyte fuel cells (PEFCs) and can be grouped using the following dichotomies: beginning-of-life (BOL) vs. long-term, membrane vs. electrode, and reversible vs. irreversible. Most impurities that impact BOL performance affect the electrode of PEFCs. CO, H₂S, and SO_x are impurities found in reformat H₂ feedstock and are known to poison the electrode, reducing cell performance in concentrations of 10ppm or less [9,10]. CO contamination is electrochemically reversible [11], but H₂S and SO_x can irreversibly induce cell failure [11,12].

Transition metal impurities are known to affect ionomer performance in the short and long term. Cations leeching into the fuel and oxidizer streams from component corrosion compete with protons at the ionomer interfaces, reducing effective ionic conductivity and incurring voltage losses [13].

In polymer electrolyte fuel cell (PEFC) systems, the long-term effects of cations are associated with irreversible membrane degradation. The fluorinated backbone of the perfluorosulfonated membrane is subject to chemical attack by H₂O₂ produced in the presence of transition metal impurities, thus degrading the membrane over time [14].

Since VRFBs typically utilize this variety of membrane, cation contamination may carry significant ramifications in VRFB operation. Fouling of membranes by vanadium species has been investigated [15,16], but currently there is little work addressing membrane degradation due to impurities.

The most harmful BOL impurity effects in PEFCs concern the platinum in the catalyst layer [17]. Since platinum is not typically used in VRFBs, comparing performance degradation mechanisms between PEFCs and VRFBs is challenging. However, some research has been done to study impurity effects. Combinations of Si and NH₄ impurities have been shown to have a significant impact on VRFB lifetime [18], but investigations of the individual effects of these impurities have not been pursued. Other research has studied compounds as VRFB additives. Several acids

have been shown to increase electrolyte stability and also improve kinetics via adsorption of functional groups on the electrode surface [19–28]. Several alcohols have been used to the same effect, adding –OH functional groups [21,29,30]. Patented work shows that adding certain transition metals to the catholyte can enhance kinetics and stability while adding certain transition metals to the anolyte can suppress hydrogen evolution [31]. The mechanism for kinetic improvement on the positive side and hydrogen suppression on the negative side is understood to be electrodeposition of the additives on the electrode surface, typically a detrimental phenomenon in PEFCs. Adding trishydroxymethyl aminomethane was shown to reduce charging and discharging overpotentials while also suppressing capacity decline with cycling [32] This effect is hypothesized to be due to –OH and –NH₂ groups bonding to the electrode, providing more active sites for redox reactions to take place. Trishydroxymethyl aminomethane was shown to improve thermal stability of V(V) and electrochemical activity [33] Adding sodium pyrophosphate tetrabasic was shown to improve electrolyte stability, dramatically reducing capacity fade with cycling [34].

Alternatively, some additives carried negative effects. Diethylenetriaminepentaacetic acid bonded to the electroactive species in such a way that the redox couples appeared irreversible in cyclic voltammograms, reducing cell performance and efficiency. Many additives have shown that their effects have limits and adding too much can have harmful impacts on the battery. Adding more than 4% L-glutamic acid reduced current generated due to adsorption to vanadium ions, inducing mass transport losses [23]. Adding Cr³⁺ to the anolyte can improve battery performance by increasing current output and redox couple reversibility, but excessive amounts will increase cell impedance [35]. L-glutamate improved thermal stability of V(V) and electrochemical activity while L-arginine worsened thermal stability but improved electrochemical activity [36].

While the goals of previous research have been different, they all revolve around the central issue that impurities, whether they are desired or not, can have a significant impact on how a battery performs, and in many cases small concentrations are required to produce an effect.

The literature provides several examples of why understanding impurities is important. Based on what has been seen so far in fuel cells and RFBs, answering the questions of which impurities are

tolerable and why can provide a means to a more functional and cheaper battery. However, providing answers to these questions is difficult given the current methods of approach used. Since impurities can have effects in small concentrations, consistency in standard solutions is important. While it is known that impurities affect VRFB performance, there are currently no associations between cell performance and a level of electrolyte reagent purity. Since electrolyte purity is directly related to cost, identifying which components are affected by impurities with BOL effects and mitigating these effects are critical issues, and are therefore the motivation of this work. The remaining aspects of impurity contamination are not covered in this work.

Chapter 3: Method of Approach

All tests were performed using a cell comprised of graphite flow plates, a single layer of 5cm² heat-treated 10AA carbon paper (0.41mm thickness, SGL) on the positive and negative sides of the battery, and a Nafion®-117 membrane. The cell architecture used is similar to fuel cell hardware with serpentine flow fields and has been discussed in the literature [37–39]. Before impurities were examined individually, vanadyl sulfate from three suppliers was obtained and tested for consistency between commercial vanadyl sulfate sources. Electrolyte solutions were made using VOSO₄ supplied by American Elements (99% purity), Alfa-Aesar (99.9% purity), and Sigma-Aldrich (99.99% purity). Solutions of 1M V(IV) and 6 M total SO₄²⁻ were mixed in accordance with standard procedure, detailed in the literature [39]. The impurities identified and analyzed by each supplier are listed in Table 1, and price per gram of vanadium (C_V) is presented under the supplier name in parentheses. Cost was determined using experimental data and the following equation:

$$C_V = \frac{C_H m_H n F}{Q MW_V}$$

where C_H is the cost of hydrate, m_H is the mass of hydrate, n is the number of electrons exchanged in the reaction, F is Faraday's constant, Q is the charge added to the electrolyte, and MW_V is molecular weight of vanadium.

Different membranes and electrodes were used for each electrolyte solution to avoid the possibility of cross-contamination. The cell was held at a constant temperature and flow rate of 30 °C and 90 mL/min during testing, respectively. Measurements were taken with a BioLogic SP-240 potentiostat.

Electrolyte was charged using 50mL on the negative side and 100 mL on the positive side. A current of 1 A was applied to the cell until a potential of 1.7V was reached. The cell continued to charge at 1.7 V until the current fell below 20 mA. Experimental concentrations were determined based on charge capacity of the electrolytes. If experimental vanadium molarities varied by more than 50 mM from 1 M, fresh electrolyte was mixed incorporating a correction factor to obtain

Table 3.1: VOSO₄ impurities by supplier

	American Element (\$3.52/g V)	Alfa-Aesar (\$4.10/g V)	Sigma-Aldrich (\$27.86/g V)
Na	30ppm	-	0.5ppm
K	20ppm	-	-
Cs	-	-	0.4ppm
Mg	-	<4ppm	-
Ca	-	560ppm	-
Sr	-	-	0.2ppm
Cr	-	-	1.0ppm
Fe	220ppm	<4ppm	1.9ppm
Cu	-	23ppm	-
Zn	-	-	5.1ppm
Mo	-	-	0.5ppm
W	-	-	0.2ppm
Yb	-	-	0.2ppm
Al	-	170ppm	-
Pb	-	-	0.7ppm
B	-	-	0.6ppm
Si	-	<4ppm	-
Sb	-	-	0.3ppm

experimental concentrations within 50 mM of 1 M. Before testing, both sides of the fully charged cell were brought to equal volume. The cell was then discharged to 50% state of charge (SOC) based on charge capacity.

Two procedures were used for collecting polarization curves: a discharge polarization curve to identify the actual limiting current density and an interleaved charge-discharge polarization curve to obtain voltage efficiencies. The first procedure entailed discharging the cell at a given current density for 30 s. The steady-state potential and current density were averaged over the last 15 s for the reported data. Each polarization step was followed by electrochemical impedance spectroscopy (EIS) from 50 Hz to 50 kHz to determine the high frequency resistance (HFR), which was used to iR -correct the cell voltage for membrane resistance at each polarization step. Current amplitudes were held at 5% of the steady-state value. The open-circuit voltage (OCV) was then maintained for 30 s followed by a cell recharge at 1.7 V until the charge added to the electrolyte closely matched the charge removed by the polarization and EIS steps. OCV was held for 30 s to check SOC before repeating the procedure in increments of $40\text{mA}/\text{cm}^2$ until the cell potential reached 0.2 V. The difference in SOC before and after the polarization curve was calculated to be 0.4% based on charge passed.

The second procedure included a discharging polarization step for 30 s, followed by EIS, and a 30 s rest at OCV. The cell was then charged at the same current density until the electrolyte reached 50% SOC. Then a charging polarization step was applied for 30 s, followed by EIS, and OCV for 30 s. The cell was then discharged back to 50% SOC. The polarization steps were repeated in increments of $40\text{mA}/\text{cm}^2$ until the potential reached 1.9 V during the charging step.

The battery was then discharged at $200\text{mA}/\text{cm}^2$ until the cell voltage reached 0.2 V. The cell was cycled $10\times$ at $200\text{mA}/\text{cm}^2$ with cutoff potentials of 0.2 V and 1.7 V. To ensure the data obtained were repeatable, fresh electrolyte from each source was tested three times. Once testing was complete, the electrolytes were combined, yielding 100 mL of 1 M vanadium comprised of half V(III) and half V(IV). The solution was then split in half and returned to the cell electrolyte tanks. The cell was removed and the electrodes were replaced with fresh heat-treated 10AA. Used electrodes were stored in deionized water. Electrolyte was run through the cell and recharged followed by another set of tests. Electrolyte rebalance, electrode replacement, and

performance tests were repeated two additional times. Scanning electron micrograms (SEM) of the electrodes were collected using a Hitachi TM-3000 (Japan) with an acceleration voltage of 15keV.

Fresh low purity electrolyte was filtered by building a cell with two serpentine graphite plates separated by a carbon paper electrode nested in a PTFE gasket. The electrolyte was sent into one graphite plate where it was forced through the electrode and left the cell through the other graphite plate. The conductive carbon paper was examined using SEM-EDS to characterize the surface. Once the surface was characterized, further filtration was done using a Buchner funnel and glass fiber filter paper with a pore size of 1 μm . The pore size was chosen such that it was close to the smallest pore sizes found in 10AA carbon paper [40].

Initial testing confirmed changes in performance due to impurities and incentivized further testing to understand how individual impurities affect performance. Some preliminary investigation was done to this end. Since concentrations were small and performance effects were difficult to isolate, large quantities of impurities were added to electrolyte solutions to magnify impurity effects. Impurity effects were seen with concentrations on the order of 10 to 100 ppm in the literature, so 1 weight percent of any impurity was assumed to be enough to produce observable effects. Cationic impurities were obtained as sulfate salts to ensure any observed effects would be associated with the impurity in question. The mass of impurity was measured using the mass of the vanadyl sulfate hydrate and the cationic impurity. The tested impurities consisted of calcium and iron. Initially, impurities were tested using the same protocol used for testing different suppliers. Effects were not seen with only ten cycles so the protocol was modified to include 50 cycles instead of 10. Increasing the number of cycles resulted in V(III) precipitation due to increased residence time. Subsequent testing consisted of charging the electrolyte as described, discharging the electrolyte until the cell reached a voltage of 0.2 V, and recharging to a cell voltage of 1.65 V. Discharge polarization steps were performed as described followed by ten cycles operating between 0.2 V and 1.65 V. Discharge polarization steps were performed every ten cycles. The cycling current density was lowered from 200 mA/cm^2 to 100 mA/cm^2 . This resulted in capacity utilization increasing from ~40% to ~95% which proved to be an effective means of preventing V(III) precipitation. Magnetic stir bars were used in an attempt

to improve electrolyte circulation through the cell, reducing residence time of V(III), but some precipitation was still observed.

Chapter 4: Results and Discussion

4.1 Discharge Polarization Curve

Discharge polarization curves were used as a means of diagnosing BOL performance of each VOSO_4 source, as shown in Figure 4.1.1a. Discrepancies in cell performance are attributed to impurities in the electrolyte since experimental molarities were corrected within 5% of one another. The purest electrolyte (Sigma-Aldrich) resulted in the highest performance, while the least pure electrolyte (American Elements) yielded the lowest performance. At a cell potential of 1.23V, the average current densities found using Sigma-Aldrich, Alfa-Aesar, and American Elements were ca. 560, 440, and 280mA/cm², respectively. Table 1 shows that VOSO_4 provided by Sigma-Aldrich is the most rigorously tested for impurities. In each case, the impurities listed are the only impurities analyzed; others may exist. The largest variation in BOL performance was observed in the mass transport region of the polarization curve, which may indicate that impurities are getting trapped in the electrodes, inhibiting reactant transport through the electrodes.

Voltage efficiencies as a function of current density (Figure 1b) were obtained for each supplier using the interleaved polarization procedure. The steepest drop in voltage efficiency with current density was observed using American Element electrolyte, due to either higher concentrations of known impurities or unknown quantities of impurities that are not accounted for. HFR did not change appreciably between suppliers, which suggests the BOL performance drop is likely due to reduced transport through the electrode. To validate these hypotheses, SEM-EDS was performed on the electrodes and is shown in Figure 4.2.

Figures 4.1.2a and 4.1.2b show deposited material on the electrode fibers exposed to American Element electrolyte. The EDS analysis shown in Figure 4.1.2c indicated that this material is predominantly Si. No particulates were found on electrodes exposed to electrolytes from other suppliers, although Alfa-Aesar electrolyte yielded lower performance than Sigma-Aldrich. VOSO_4 supplied by Alfa-Aesar reported Si concentrations below 4ppm, which suggests that even low concentrations have noticeable effects on performance. A possible reason that Si was not observed on electrodes exposed to Alfa-Aesar electrolyte using SEM is the low concentration

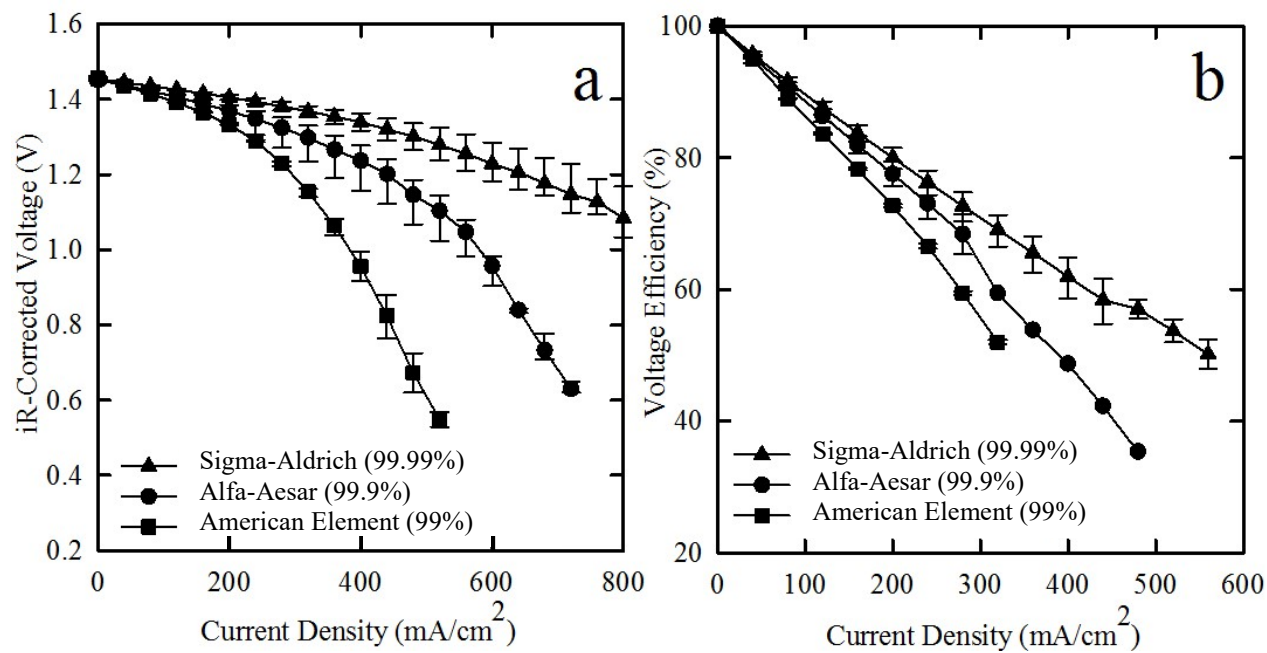


Figure 4.1.1: BOL polarization curves (a) and voltage efficiencies (b) at 50% SOC of 1M VOSO_4 in 5M H_2SO_4 with multiple suppliers

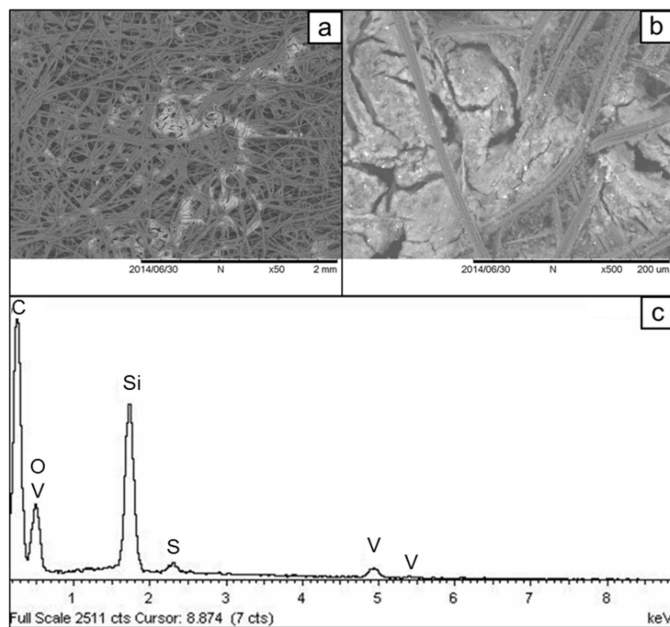


Figure 4.1.2: SEM image of electrode exposed to American Elements electrolyte during testing at 50× (a) and 500× (b) magnification with EDS analysis of electrode (c).

of Si was deposited within the electrode, but did not agglomerate on the surface. Assuming the mass change of the electrodes exposed to American Element electrolyte is attributable to Si depositions, a concentration of 13.6 ppm is estimated. In this concentration range, it is possible that Si is deposited throughout the electrode and is easier to detect.

Based on the polarization curves, it was concluded that Si fouling blocks active sites and reactant transport which supports the posed hypotheses and helps explain the variation in BOL performance found using electrolytes from different sources. Published work also shows that mechanical filtration removes Si from the electrolyte and significantly improves performance [18], which supports the EDS analysis.

4.2 Short-Term Battery Cycling

Over 10 cycles, the coulombic efficiencies of all VOSO₄ suppliers remain close to 99%. No trends in coulombic efficiency were observed with respect to cycle number. At high enough rates, crossover would exacerbate voltage efficiency loss with increasing current density and would reduce cell performance in the mass transport regime. Since crossover effects are small within the range of data analyzed, these phenomena are not of concern here.

In addition to cell power density, impurities also affect the overall capacity of the battery, as shown in Figure 4.2.1. The discharge times for a typical Sigma-Aldrich, Alfa-Aesar, and American Elements, cycle were 3227s, 2945s, and 1672s, respectively. A small part of the variation in performance is associated with different areal-specific resistances between membranes, since a different membrane was used for each VOSO₄ supplier. The average areal-specific resistance between the nine tests performed was 547mOhm·cm² and varied by no more than 60mOhm·cm² at a discharge current density of 200mA/cm², accounting for at most a 12mV variation.

The patented work by Kubata et al. shows an increase in cell resistance in the presence of impurities, which was not observed in this work. Cell resistance changes were found using electrolyte containing Si >40ppm and NH₄ = 18ppm [18] which suggests that the observed Si concentration of 13.6ppm should not noticeably affect cell resistance. The fact that NH₄ was not

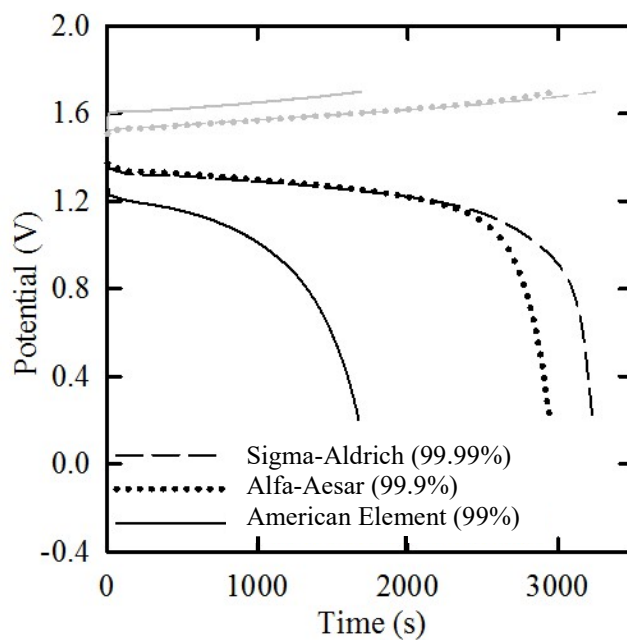


Figure 4.2.1: Charge-discharge curves of different suppliers of VOSO_4 . Gray indicates charge, black indicates discharge.

incorporated into this study and no trends in HFR were observed between tests or cycles reinforces this conclusion as NH_4 magnifies Si effects on cell resistance [18]. Thus, membrane degradation was ruled out as an operative loss mechanism.

Obtaining polarization curves with new electrodes on used electrodes provided insight into reported electrode blockage. The results are shown in Figure 4.2.2. After remixing electrolyte and changing electrodes, performance was seen to improve significantly. Subsequent electrolyte remixing and electrode replacements did not show significant improvement. The large improvement in performance implies that the electrodes acted as a filter, permanently removing particulates from the electrolyte. SEM images of the electrodes used in the fresh solution and remixed solution polarization curves were obtained to validate this hypothesis; the comparison is presented in Figure 4.2.3, which confirms that impurities become lodged in the electrode and are removed once the electrodes are replaced. This phenomenon was seen on both the positive and negative sides of the cell, implying that this filtration was not a function of potential and that the electrodes were removing electrolyte particulates present in large enough sizes such that they become lodged in the electrodes. To investigate electrolyte filtration as an electrochemical process, fresh low purity electrolyte was fed through a test cell without running any current for 24 hours. After 24 hours had passed the cell was removed along with the electrode used for filtering which was dried in an oven at 70 °C for 24 hours. The filtered electrolyte was then run through a test cell where the testing procedure described previously was performed. The polarization curves from the filtered electrolyte are presented as part of Figure 4.2.4, which shows that filtration shows similar performance improvements to those seen by replacing electrodes after running polarization curves and cycling on a cell. These results indicate that the electrode blockage is a physical phenomenon and not electrochemical in nature. The filtration electrode was examined under SEM to understand what was filtered from the electrode. The electrode was then examined under SEM as shown in Figure 4.2.5, which shows particulate accumulation on the electrode surface. The pattern of the deposition is caused by the geometry of the serpentine flow channels that the electrolyte was filtered through. Larger quantities of agglomerate exist on the filtration electrode because 200 mL of electrolyte was passed through the electrode as opposed to the 50 mL passed over the electrode in Figure 4.2.3. Additionally, the filter cell carbon paper caught a higher percentage of the electrolyte impurities because the

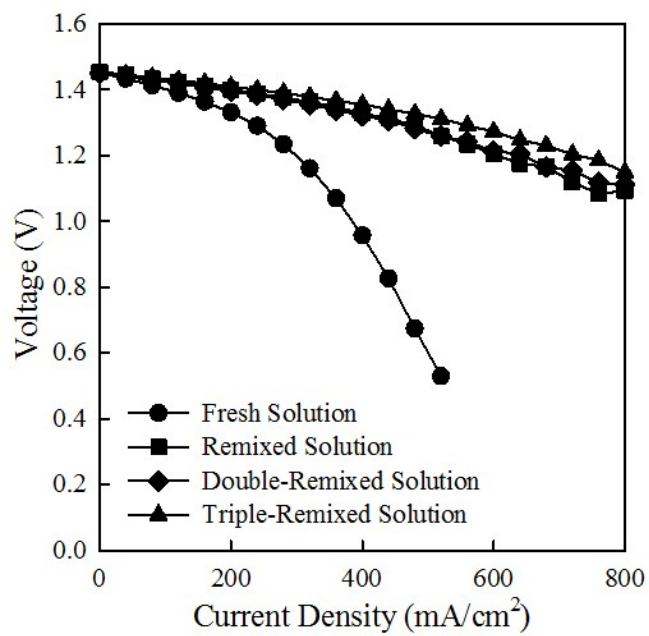


Figure 4.2.2: Polarization curves of low purity electrolyte after remixing electrolyte and replacing cell electrodes

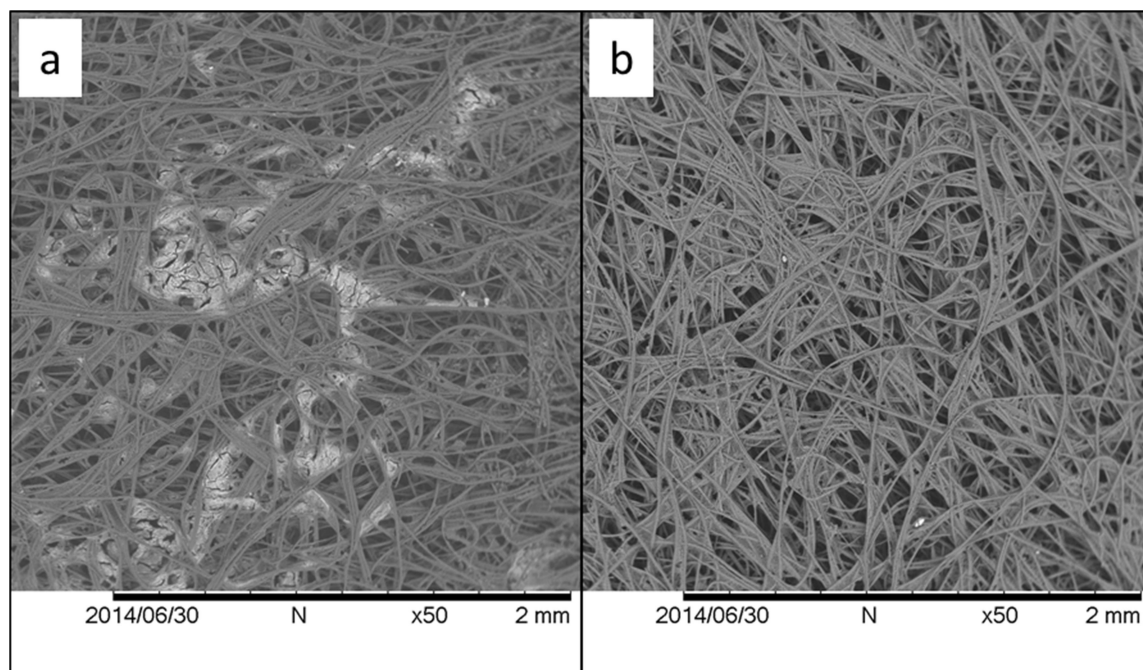


Figure 4.2.3: SEM comparison of electrodes tested in fresh (a) and remixed (b) solution

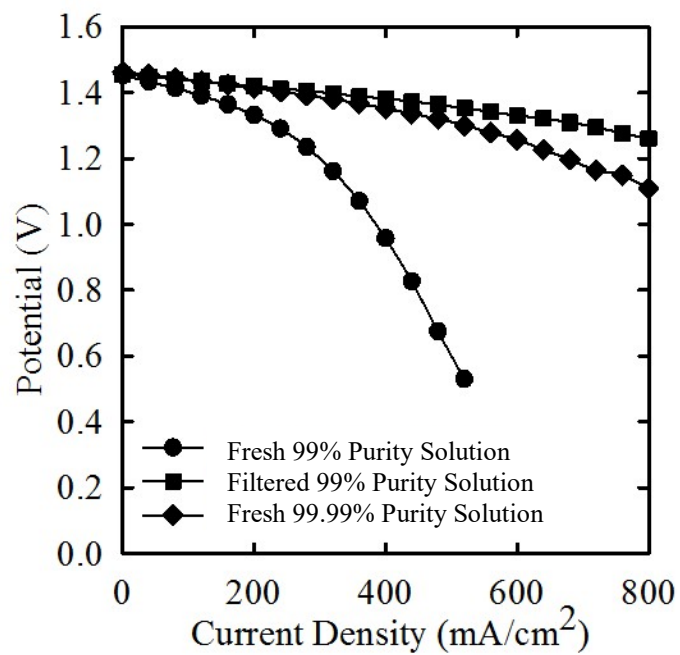


Figure 4.2.4: Polarization curves of fresh low purity, filtered low purity, and fresh high purity electrolytes

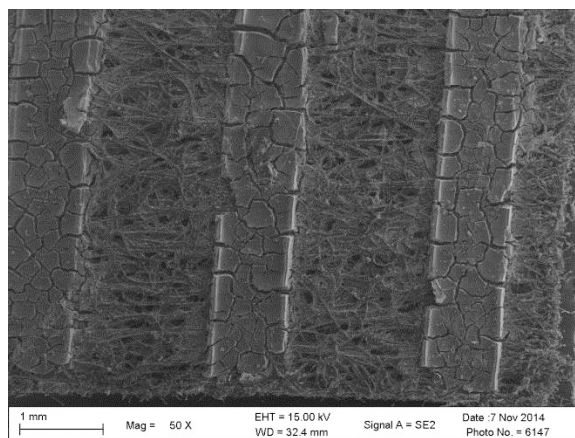


Figure 4.2.5: SEM of filter cell carbon paper

electrolyte was forced through the carbon paper instead of flowing alongside it. EDS analysis was performed on the accumulated particulate and is presented in Figure 4.2.6. Figure 4.2.6 reinforces that the agglomerate is, within the error of the instrument, entirely comprised of silicon. Given what is known about the electrolyte and the carbon paper, the phase of the silicon can be inferred from the calculated atomic weight percent of the elements found in the EDS analysis. The carbon mixed with the agglomerate is likely residual carbon powder removed from the electrode as electrolyte passed through and deposited on top of the silicon as it was recirculated back through the cell. The carbon papers have been characterized previously as at least 99% carbon which implies that the other elements found in the analysis should not share any bonds with carbon. The vanadium and sulfur found in the EDS analysis are assumed to be from the electrolyte as parts of vanadyl and sulfate ions, which carry one and four oxygen atoms respectively. The remaining oxygen is then assumed to be adhered to silicon as SiO_2 forming silica. The atomic percent of oxygen that would be expected by the assumed distribution was calculated to be 62.59%, which matches the 62.88% reported by EDS within the uncertainty of the analysis.

4.3 Cationic Impurities

Once silica was identified, effects of cationic impurities were sought. Low purity American Element solution was filtered and known amounts of desired impurities were added. Calcium was the first impurity investigated and was added to electrolyte as CaSO_4 . 200 mL of electrolyte was made from 47.64 g of VOSO_4 . The 0.47 g of Ca corresponding to 1 wt% of the VOSO_4 powder was added as 1.62 g of CaSO_4 . Similarly, 1 wt% Fe was added to solution by adding 2.37 g FeSO_4 hepta-hydrate. Preliminary polarization curves were obtained and are shown in Figure 4.3.1.

CaSO_4 was insoluble and had no visible impact on cell performance, producing polarization curves that were within experimental error of filtered solution polarization curves. Fouling electrolyte with iron seemed to induce an effect, but not as much in the expected regimes of the polarization curve. A BOL effect from cationic impurities would be expected to be manifested at lower current densities, in the kinetic and ohmic regimes as opposed to the mass transport

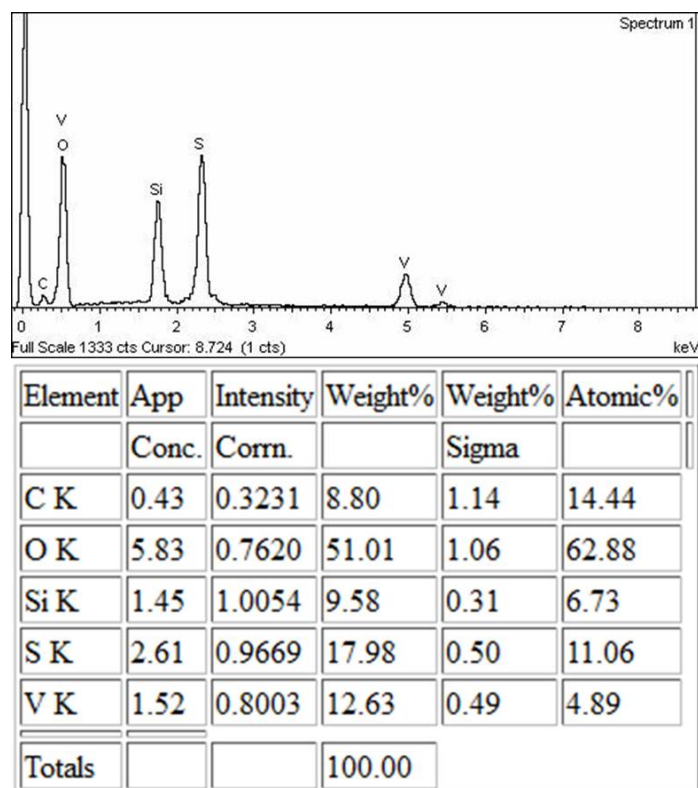


Figure 4.2.6: EDS analysis of particulate

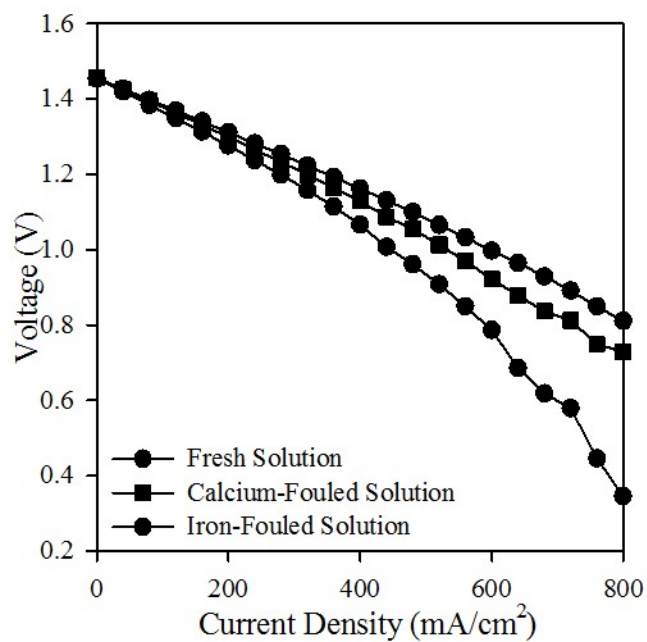


Figure 4.3.1: Polarization Curves using filtered, calcium-fouled, and iron-fouled electrolytes

regime. Changes in membrane resistance are difficult to detect in polarization curves at lower current densities because lower current causes the losses from membrane resistance to be smaller. At the higher current densities these losses would be magnified, showing an effect similar to what was seen in Figure 9. Iron was added to higher-purity Alfa-Aesar solution and longer-term testing was performed to determine if the effects observed were indeed caused by iron.

Fresh electrolyte and iron-fouled electrolyte were tested over the course of 50 cycles. After ten cycles, polarization curves were taken. The polarization curves looked similar to those shown in Figure 9. For readability, the current produced at 1.2 V every ten cycles is shown in Figure 4.3.2. Since the polarization curves related to Figure 4.3.2 were taken at a higher state of charge as described in **Method of Approach**, the voltages seen are significantly higher than those seen with the 50% SOC polarization curves. Interestingly, the current density is lower for iron-fouled solution initially, but iron-fouled solution retains its performance better than fresh solution. It is understood that cationic impurities' primary impacts are on the membrane, so the development of HFR over the course of cycling was examined and is presented in Figure 4.3.3. Figure 4.3.3 exhibits a similar trend to Figure 4.3.2, in that the iron-fouled solution exhibits worse performance initially but the performance decay is better compared to fresh solution. Though this difference in resistance is small, it is worth considering that this phenomenon could be a result of iron molecules blocking the membrane to a lesser degree than vanadium, allowing more protons to pass through the membrane than a vanadium molecule would at the same site. Whatever the case, with lower HFR come lower ohmic losses.

Since the cycling conditions are well within the ohmic region, any membrane changes should show up in cycling performance. The changes seen were small, however, and hence are difficult to ascribe to any one aspect of battery performance. The improved power retention offers a partial explanation of the apparently improved cycle performance of vanadium-fouled electrolyte, but if the reduced resistance of iron-fouled electrolyte also leads to increased overpotentials, battery efficiency may not improve and thus the reduced resistance is not helpful. The overall efficiencies of the two solutions were calculated over the course of cycling and are presented in Figure 4.3.4 which shows similar trends to the previous figures and also gives those

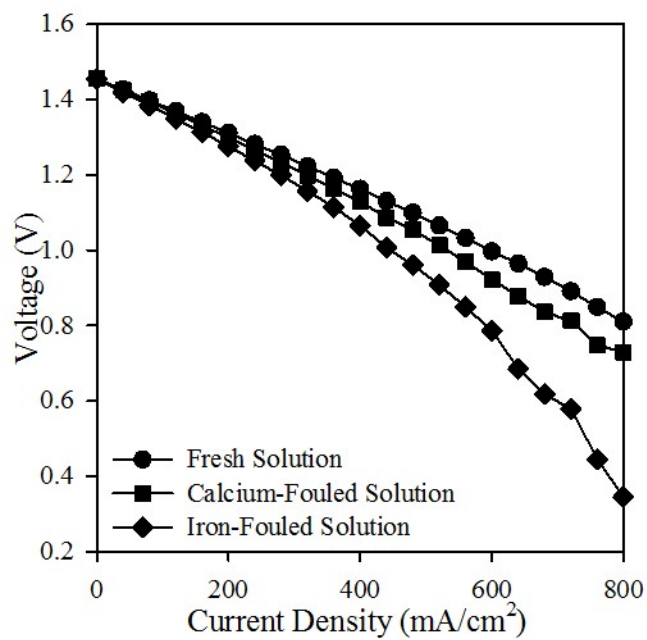


Figure 4.3.2: Current Densities for fresh and iron-fouled solutions at a potential of 1.2 volts taken every ten cycles

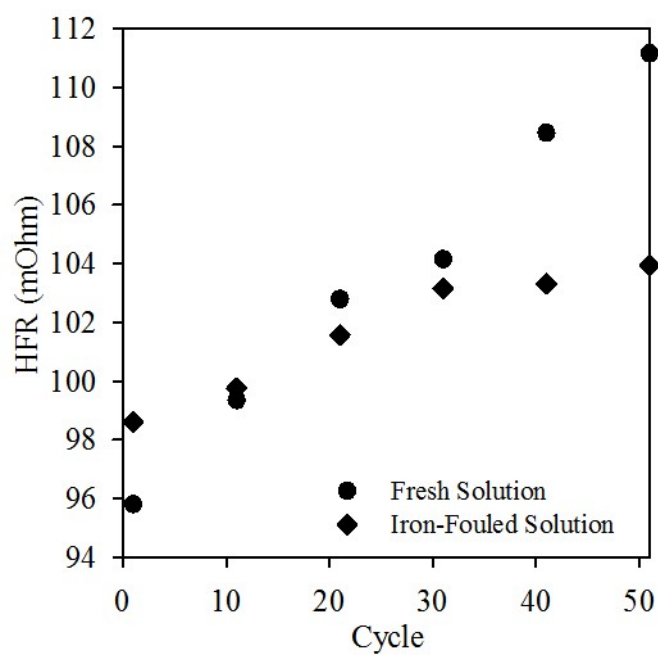


Figure 4.3.3: Evolution of HFR for fresh and iron-fouled solution as a function of cycle

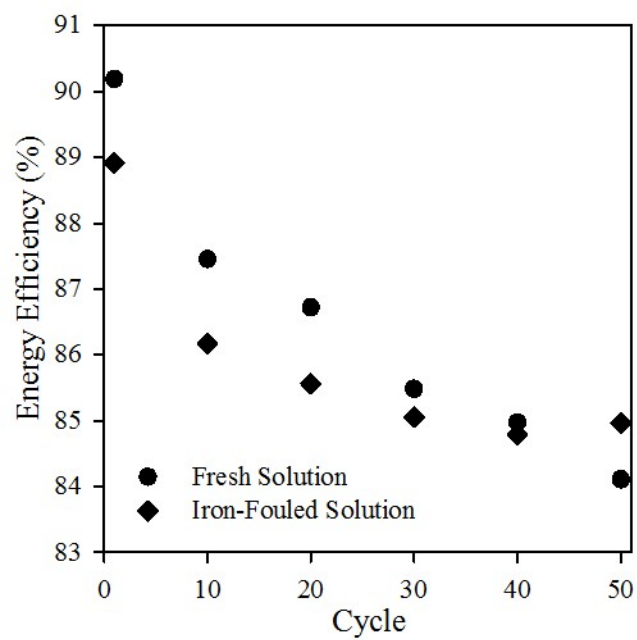


Figure 4.3.4: Development of energy efficiency voltage with cycle

trends a sense of scale. While performance may be negatively impacted by using iron-fouled electrolyte, the impacts observed were miniscule, yielding at most a 1 % change in overall cell efficiency. Near the end of the cycling done, the efficiency was even seen to surpass that of fresh solution by a narrow margin. These margins are so small that it is still difficult to determine whether or not iron has an effect on battery performance, even at 1 wt %. This suggests that, as an impurity, iron is of little concern.

Chapter 5: Conclusions and Future Work

Significant differences in beginning-of-life (BOL) performance were observed using different suppliers of VOSO_4 . Lower purity reagents carried significant influence on BOL performance and voltage efficiency. It was found that Si present in commercial VOSO_4 supply accumulates on the electrodes, inhibiting mass transport and reducing the operational window and capacity of the battery. While using lower purity electrolyte may be less expensive, cost per kilowatt-hour increases due to increased overpotentials that yield less available battery capacity. Electrolyte filtration was found to be an effective means of bringing low purity electrolyte performance to levels seen with the most pure solutions used, representing an enormous cost savings compared to using higher purity solutions.

Preliminary investigation of the effects of impurity additives showed that VRFBs are resilient to iron-fouling. 1 wt % iron had little impact on performance, suggesting that looser restrictions may be a viable means of significantly reducing electrolyte costs. While further testing should be pursued, if the HFR difference between iron-fouled and fresh solution becomes significant with cycling, adding iron would improve VRFB performance.

Future work would first and foremost comprise a more comprehensive study of iron to use as a template for work with future impurities. First, adding iron to saturation should be considered, as relatively high weight percents of other impurities may carry little impact. Second, since a real battery installation will likely use a wider window of current densities than those explored here, a more parametric study should be performed using multiple regions of the kinetic, ohmic, and mass transport regimes. This would provide an understanding of how impurities limit the operational window of the battery, which would be a more useful analysis for VRFB viability. Third, the gentler increase in HFR with cycling is compelling and warrants further investigation. Other transition and alkali metals should be investigated to better understand whether or not this effect is a function of effective molecular radius, electronegativity, or some other aspect of the molecular interactions between the electrolyte ions and the battery membrane. Fourth, any impurity effects should be investigated such that their effects are identified as being electrochemically induced, caused by electro-osmotic migration of the ions through the membrane, or caused simply by free diffusion of impurities into the membrane.

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Vita

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