Elucidating Effects of Faradaic Imbalance on Vanadium Redox Flow Battery Performance: Experimental Characterization

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Long-term performance and lifetime of vanadium redox flow batteries (VRFBs) are critical metrics in widespread implementation of this technology. One challenging issue that negatively affects these parameters is the faradaic imbalance, which is not comprehensively investigated in the literature. Faradaic imbalance is known as the shift in the average oxidation state (AOS) of the electrolyte due to side reactions. This type of imbalance requires chemical/electrochemical mitigation rather than simple electrolyte remixing. Herein, we investigate faradaic imbalance by preparing unbalanced electrolytes with different AOS values. The performance characteristics of the flow cell utilizing electrolytes with different AOS values are reported. Based on the results of charge-discharge cycling, polarization testing, and electrochemical impedance spectroscopy measurements, faradaic imbalance is found to significantly affect discharge capacity, maximum power density, cell resistances, and efficiency values. While the ratio of discharge capacity to theoretical capacity is 83% for the ideally balanced case (AOS 3.5+), it drops to 53.4% for the AOS 3.9+ case. Additionally, there is a substantial decrease of 44% in the maximum available power density for the most unbalanced case. This noticeable performance degradation highlights the importance of faradaic imbalance as a critical factor which requires further attention especially during extended cycling.

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Renewable energy sources (e.g., wind and solar) are progressively being deployed worldwide in order to eliminate the negative environmental impact of fossil fuels. However, the intermittent nature of these sources makes it necessary to develop effective large-scale energy storage devices which can level renewable energy output over time. In this regard, redox flow batteries (RFBs) have gained increasing attention as grid-scale energy storage systems. The unique characteristic of RFBs is their ability to decouple power and energy ratings, which makes them more flexible, modular and economically scalable compared to conventional rechargeable batteries. While the electrolyte, which is stored in external reservoirs and pumped to the flow cell, determines the energy storage capacity, the flow cell, where electrochemical reaction occurs, dictates the power rating of the cell. Among the RFBs proposed to date, vanadium redox flow battery (VRFB) is one of the most widely studied and commercially available flow battery systems. In contrast with other flow battery chemistries such as Zn-Br and Fe-Cr, VRFBs exploit different oxidation states of the same element, vanadium, as both positive and negative active materials, and consequently they do not suffer from electrolyte cross-contamination. Redox reactions occurring in each half-cell of the VRFB and the whole cell are given in Equations 1–3:

Cathode: \[ \text{VO}^{2+} + 2H_2O \rightarrow \text{VO}_2^+ + 2H^+ + 2e^- \Delta \text{E}^- = 0.99 \text{ V vs SHE} \] [1]

Anode: \[ V^{3+} + e^- \leftrightarrow V^{2+} \] [2]

Cell: \[ \text{V}O^{2+} + 2H_2O \rightarrow \text{VO}_2^+ + 2H^+ + 2e^- \Delta \text{E}^- = 1.25 \text{ V vs SHE} \] [3]

Despite the advantages of VRFBs, the long-term performance and cycle life of these systems are restricted by the loss of available energy capacity (i.e., capacity fade). The capacity fade observed in a flow battery can be partially attributed to the crossover issue which is described as the undesired transfer of vanadium ions through the membrane. As a result of crossover, various side reactions and self-discharge reactions occur in both half-cells of the battery, leading to a decrease in the coulombic efficiency and available capacity. During long-term cycling, crossover leads to concentration imbalance of the electrolyte which we refer to as ‘stoichiometric imbalance’. Along with the undesired transfer of vanadium ions, water can also transport across the membrane due to either osmosis or electroosmotic drag, resulting in stoichiometric and volumetric imbalance of the electrolyte. While stoichiometric and volumetric imbalances are critical issues that can cause failure of the system over long-term cycling, various methods to monitor and mitigate these types of imbalance and the associated negative effects (e.g., capacity fade and performance degradation) have been widely reported in the literature. In one of the early studies focusing on vanadium crossover, the VRFB operation was simulated using a 2-D transient model incorporating the transport of all species (i.e., vanadium, water, hydrogen ions, and bisulfate) as a result of all three modes of species transport mechanisms (i.e., convection, diffusion, and migration), and the crossover-related side reactions. The charge/discharge cycling simulations reported in this study indicated that the net transfer of vanadium from the ‘+’ to ‘−’ half-cell was the primary cause of the capacity loss for the cells with Nafion membranes. It was suggested that the direction and magnitude of crossover were mainly dependent on the operating conditions and membrane transport parameters used in the simulation. Soon after, the same research group conducted another modeling study in which they have further studied the species transport mechanisms governing capacity loss in two different types of proton exchange membranes (Sulfonated-Radel and Nafion 117). Based on this investigation, for convection-dominated membranes such as sulfonated-Radel, the direction of electro-osmotic convection during charge and discharge steps was reversed, and found to result in a significantly lower net crossover when compared to Nafion. In addition to the studies aimed at establishing a fundamental understanding of the crossover phenomenon, various mitigation techniques were proposed to minimize crossover and its negative effects. One of the introduced methods was applying asymmetric current to mitigate the crossover and increase the lifespan of a VRFB. It was depicted that for both diffusion-dominated and convection-dominated membranes asymmetrically increasing the charging current density decreases the net convective crossover of the bulk electrolyte, which leads to a reduction in the magnitude of net crossover. This observation was attributed to the fact that electro-osmotic convection during charging is enhanced by increasing the charging current. This increased electro-osmotic convection compensates convective crossover that occurs due to osmosis toward the opposite direction over the end of full cycle. In addition, utilizing a thicker membrane was suggested to effectively reduce the rate of capacity fade associated with the crossover over time (up to ~15%) at the expense of reducing the energy efficiency (up to ~2%) due to increased ohmic losses. Different methods, such as tuning the pressure of the positive and negative electrolytes, employing asymmetric electrolyte volumes, and synthesizing different...
kinds of membranes (such as amphoteric or polysulfide-based cross-linked AEMs) have been explored as well to alleviate the crossover issue.

Furthermore, the literature offers several methods to correct stoichiometric imbalance and minimize the associated negative effects. Remixing is probably the simplest and most cost-effective method, which is defined as the complete mixing of positive and negative electrolytes and equally splitting the mixed solution into two half-cells. Another method which is similar to the remixing is reflowing the electrolyte. This method is based on allowing the electrolyte to transfer automatically and periodically from one reservoir into the other reservoir. According to a recent study, reflowing method can markedly prolong the cycle life of the flow battery by compensating the capacity decay. Considering the end-of-life of a VRFB to be when the discharge capacity decreases to 45% of the theoretical capacity, the lifespan of the battery was enhanced from 206 to 466 cycles after implementing the reflow method. Another type of reflowing method was introduced by Schafner et al. in which electrolyte overflows continuously from the positive to the negative side. Although this method keeps the electrolyte capacity more balanced, electrolyte stability is a limiting factor for that since the concentration of vanadium and sulfate ions are affected by continuous overflow.

Along with the stoichiometric imbalance, there is another type of electrolyte imbalance which is referred as faradaic imbalance. Two separate phenomena contribute primarily to faradaic imbalance:

i. Gassing side reactions occurring at both negative and positive electrodes:

   a) Hydrogen evolution reaction (HER) at the negative electrode:
   \[ 2H^+ + 2e^- \rightarrow H_2 + \triangle E^\circ = 0.00 \text{ V vs SHE} \]  

The electrochemical potential of the negative electrode in a VRFB is below the standard potential for hydrogen evolution, and thermodynamically a more negative potential leads to simultaneous HER and V^3+ reduction reaction at the negative electrode. In fact, hydrogen evolution is always a possibility during normal operation of a VRFB except at extremely low state of charge (SOC). According to the Nernst equation, the potentials of both V^2+/V^3+ and hydrogen evolution reactions are a function of different factors such as temperature, SOC, species concentration in the electrolyte (vanadium, sulfate), etc. Therefore, depending on the kinetics of these reactions, critical operating factors (e.g., SOC) can be quantified, beyond which HER is aggravated. For example, unlike VRFBs, high cell potential is a less critical issue for alkaline or lead acid batteries in terms of water electrolysis. In these batteries, electrodes at the respective pH values are not efficient catalysts for the electrolysis reaction. Therefore, electrode kinetics are considered as a critical factor affecting a systems tendency toward faradaic imbalance. Hydrogen evolution, as a parasitic side reaction, adversely affects the battery performance in different ways. First, it consumes a portion of the charge current and may block reaction sites on the electrode, leading to decrease in coulombic and energy efficiencies. Then, HER impacts vanadium ion valence in negative electrolyte and consequently, it causes unbalanced valence of vanadium ions in positive and negative electrolytes which results in capacity degradation. Furthermore, this side reaction disturbs the SOC balance in both half-cells and makes it necessary to restrict reaching high SOC values to avoid further capacity fade of the battery due to accelerated hydrogen evolution rate.

b) Oxygen evolution reaction at the positive electrode:
   \[ 2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \Delta E^\circ = 1.23 \text{ V vs SHE} \]  

Two factors primarily contribute to oxygen evolution side reaction: overcharging and the amount of oxygen-containing functional groups of the electrode. Overcharging the cell results in water electrolysis and associated oxygen and hydrogen evolution side reactions in negative and positive half-cells respectively. Moreover, –COOH and –C=O functional groups in the electrode auto-catalytically promote oxygen evolution side reaction which gets even more aggravated at high SOCs. The O_2 evolution reaction consumes a portion of the applied current, decreasing the amount of current available for V^{4+} oxidation. This will subsequently lead to faradaic imbalance and associated capacity degradation of the VRFB.

ii. Air oxidation of bivalent vanadium ion (V^{2+}) in the negative side:
   \[ O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O + 4V^{3+} \]  

Air oxidation of V^{2+} ions occurs in both the negative reservoir and the negative side of the cell stack. In both cases, V^{2+} is oxidized without a corresponding reduction of V^{4+} on the positive side of the cell which leads to faradaic imbalance increasing the AOS value. Although this side reaction can be retarded by utilizing a higher concentration of vanadium and sulfuric acid, appropriate design of the external tank, and purging inert gas into the negative tank, it could be difficult to completely be eliminated. Therefore, the associated electrolyte imbalance should be taken into account to develop more accurate maintenance schedules.

Unlike stoichiometric imbalance, faradaic imbalance caused by the above side reactions cannot be restored by simple electrolyte remixing/reflowing. In fact, for the faradaic imbalance, average oxidation state (AOS) of the battery shifts from the ideal state of V^{3.5}+ leading to a capacity fade due to the deficiency of electron donor/acceptor species. For this reason, it can only be corrected by shifting the AOS by introducing a net input/output of charge to/from the system which requires either chemical or electrochemical intervention. Chemical and electrochemical rebalancing methods, unlike remixing and reflowing, have not been studied widely in the literature and there are only a few investigations focusing on chemical rebalancing methods to alleviate the capacity degradation caused by faradaic imbalance. Roe et al. proposed a simple method for the cases when the AOS < 3.5 by introducing oxygen into the negative side to partially oxidize the V^{2+} ions until the V(II): V(III) ratio matches the V(V): V(IV) ratio in the positive side electrolyte. In another study carried out by Skyllas-Kazacos and co-workers, adding certain organic compounds to the positive electrolyte was introduced to allow the partial reduction of the V(V). In this investigation, oxalic acid, methanol, and ethanol have been suggested to be good rebalancing agents since carbon dioxide and water are the products of the rebalancing reactions, introducing no impurities in the electrolyte provided the reactions progress to completion. Self-built electrolysis cell and introducing H_2 to the positive electrolyte were also suggested in the literature to correct the faradaic imbalance. The compensation of losses through implementing electrolysis cell was realized with an efficiency up to 98%. Moreover, it was depicted that both H^+-ions losses and charge imbalance can be compensated throughout this method. In the method introducing H_2, the evolved H_2 from the parasitic reaction at the negative electrode reacts with the charged positive electrolyte. However, due to the slow rate of reaction between V^{3+} and H_2 at room temperature, catalysts are required. Unlike academic research studies, adjusting the AOS received more attention to maintain the health of the flow battery in industrial applications. Depending on the tendency of the battery to creep toward high or low AOS values, different reducing or oxidizing agents (oxalic acid, formic acid, and alcohol as reducing agents; oxygen as oxidizing agent) were suggested to add to the positive and negative side respectively to adjust the AOS.

Although these studies are great initial efforts introducing functional methods to correct the faradaic imbalance, it is still important to establish a comprehensive understanding on this unavoidable issue. More specifically, the literature does not provide the critical information on how faradaic imbalance affects the flow cell performance in terms of efficiency, capacity, and resistance values. Usually, faradaic imbalance rate changes during long-term cycling and the cell performance will vary according to the AOS. The lack of this knowledge would possibly lead to inaccurate conclusions when long-term performance is investigated. In this study, imbalanced electrolytes with different AOS values (3.5+, 3.6+, 3.7+, 3.8+, 3.9+) are prepared to experimentally simulate the faradaic imbalance phenomenon.
occurring over the long-term cycling of the VRFB. During cycling, hydrogen evolution and air oxidation of V$^{2+}$ side reactions cause a positive shift of AOS. Only oxygen evolution causes a negative shift of AOS, and is far less facile than the other side reactions mentioned above. Consequently, in practice the AOS shift occurs only to higher values. For this reason, only the AOS values greater than the ideal value of 3.5+ are investigated. In order to understand how different degrees of faradaic imbalance affect the overall flow cell performance, experimental techniques such as charge-discharge cycling, polarization curve, and electrochemical impedance spectroscopy (EIS) are carried out. Based on the results of these experiments, it is depicted how faradaic imbalance impacts various aspects of the cell performance, including cell efficiency, types of resistance, peak power density, limiting current density, and discharge capacity. The obtained data can also help with making decisions for the implementation of periodic mitigation techniques to improve the state of health of the flow battery system. A systematic maintenance plan for the flow battery which is based on the obtained data of this study can prevent possible future failure of the cell due to the imbalanced electrolyte.

Since the electrolyte cost accounts for the second highest proportion in VRFBs,40 a comprehensive plan to keep the electrolyte balanced will be a significant step to a cost-effective utilization of VRFBs specifically in large-scale cells with a great amount of electrolyte.

Method of Approach

Flow cell architecture.—The experimental setup includes a flow cell, peristaltic pumps (Masterflex L/S, Cole-Parmer, USA) for positive and negative electrolyte flow, and external reservoirs. The cell has 5 cm$^2$ active surface area. Three layers of carbon paper electrodes (Av Carb F250C, 250 μm thickness, USA) were sandwiched between the interdigitated flow plate and the membrane. Pretreated Nafion 212 served as the membrane in order to separate two sides of the cell. Pretreatment procedure included soaking the membrane in 1 M H$_2$SO$_4$ at 80°C for 30 minutes followed by immersion in deionized water at 80°C for 30 minutes. Two electrolyte reservoirs were used in conjunction with the cell stack for negative (V(II)/V(III)) and positive (V(IV)/V(V)) half-cells. 20 mL of electrolyte was stored in each external tank which consisted of 1.6 M vanadium dissolved in 2.5 M sulfuric acid. This electrolyte was pumped through the cell applying 80 mL мин$^{-1}$ flow rate. All the flow battery performance data was obtained for 5 different electrolyte samples and for each case the only difference is the V$^{2+}$/V$^{3+}$ concentration ratio in the negative side reservoir leading to 5 different average oxidation states (AOS): 3.5+, 3.6+, 3.7+, 3.8+, and 3.9+.

Electrolyte preparation.—The electrolyte was prepared by filling negative and positive reservoirs with 20 mL and 40 mL solution of 1.6 M VO(SO$_4$_2 (Sigma Aldrich, 98% purity) in 2.5 M H$_2$SO$_4$ respectively. The electrolyte solutions were charged potentiostatically at 1.8 V to produce V$^{2+}$ and V$^{3+}$ for the negative and the positive half-cell reactions, respectively. During the whole testing procedure, the negative electrolyte was stored under a continuous nitrogen gas blanket to prevent the oxidation of V$^{2+}$ ions. The electrolyte sample with AOS 3.5+ included 20 mL of V$^{2+}$ in the negative tank and 20 mL of V$^{3+}$ in the positive tank. In order to prepare the other 4 electrolyte samples with higher AOS values, V$^{2+}$ was mixed with an appropriate portion of V$^{3+}$ to get 20 mL of electrolyte in the negative side. V$^{3+}$ solution was prepared through discharging the fully charged electrolyte and removing the solution from the negative tank. For the positive side, electrolyte is the same as AOS 3.5+ case which includes 20 mL of V$^{3+}$. AOS was calculated implementing Eq. 7. To better understand the electrolyte preparation procedure, electrolyte composition is shown in Table I.

| AOS | $\frac{3}{\sum_{i=2}^{5} m_{i,(-)} \cdot z}$ |
|-----|----------------------------------------|
| 3.5+| 20 mL V$^{5+}$ 20 mL V$^{3+}$ 20 mL V$^{5+}$ 20 mL V$^{3+}$ 20 mL V$^{5+}$ |
| 3.6+| 20 mL V$^{5+}$ 16 mL V$^{3+}$ 12 mL V$^{2+}$ 8 mL V$^{2+}$ 4 mL V$^{2+}$ |
| 3.7+| 4 mL V$^{5+}$ 8 mL V$^{5+}$ 12 mL V$^{3+}$ 16 mL V$^{3+}$ |
| 3.8+| |
| 3.9+| |

Where, $m_i$ is the molarity of each vanadium ion in the electrolyte, and $z$ is the valence state of the vanadium which varies between 2 to 5. In all cases, the system has the same theoretical capacity of 857.6 mA.h.

Charge-discharge cycling.—Charge-discharge cycling was carried out to calculate both the discharge capacity and efficiency values of the flow battery. Cycling data was obtained by applying 200 mA.cm$^{-2}$ current density with 0.6–1.8 V cutoff voltages. Extended cycling was conducted applying the same current density for 16 cycles for each AOS case with the same cutoff voltages. For all the cycling experiments flow rate was held constant at 80 mL min$^{-1}$. One of the other critical parameters in evaluating the performance of a flow battery system is its efficiency values. In this regard, efficiency values were calculated from the extended charge-discharge cycling over 16 cycles for each electrolyte sample and average values were reported. Efficiency values for galvanostatic charging-discharging process were calculated using the following equations:

$$\eta_c = \frac{t_d}{t_i} \times 100\%$$ [8]

$$\eta_v = \frac{V_d}{V_i} \times 100\%$$ [9]

$$\eta_e = \eta_c \times \eta_v$$ [10]

Where $t_d$ is the discharging time, $t_i$ is the charging time, $V_d$ is the average discharging voltage, $V_i$ is the average charging voltage, and $\eta_c$, $\eta_v$, $\eta_e$ are coulombic, voltage, and energy efficiencies respectively.

Polarization curve and electrochemical impedance spectroscopy (EIS).—Polarization curve measurement is a simple and useful method through which resistance characterization of the cell can be determined. In order to obtain polarization curve, a series of galvanostatic charge-discharge steps in the range of −400 to 400 mA.m$^{-2}$ was applied to the cell with a current density step of ±40 mA.m$^{-2}$. We alternated between charge and discharge for each current density in order to keep the average SOC ~50%. For each step, the current density was held constant for 30 seconds to obtain steady-state cell potential response. The total area specific resistance (ASR) of the cell can be calculated from the slope of the polarization curve. It is also important to quantify various contributions to the ASR of the cell. Implementing an EIS experiment can provide the required data and add more detailed information to the data obtained from the polarization curve. Analysis of EIS spectra with equivalent electrical circuits can help quantify the various contributions to the overall impedance, such as ohmic, charge transfer, and mass transfer resistances. Right after the polarization curve experiment, EIS was carried out using 50% SOC electrolyte. For impedance data acquisition, 5 mV sinusoidal perturbation was implemented while setting the DC voltage to 0 V (vs. the OCV of the flow cell). Furthermore, the EIS experiment was performed in a wide frequency range of 10 mHz to 100 kHz to capture the various processes occurring within the flow cell.

Conductivity measurement.—Conductivity of each electrolyte sample was measured by H-Cell (Scribner Associates Inc.) in which Ag/AgCl served as the reference electrode (RE) and two platinum wires served as working and counter electrodes (WE, CE). For each
step, 60 mL of electrolyte was poured in the H-Cell and after connecting it to the potentiostat, conductivity was measured through implementing the linear sweep voltammetry (LSV) technique, applying the voltage range of ±0.1 V vs. OCV with the scan rate of 50 mV.s⁻¹. Conductivity was calculated using the following equation:

$$\delta_{\text{Elec}} = \frac{K_{\text{Cell}}}{R_{\text{Elec}}}$$

In which, $\delta_{\text{Elec}}$ is the electrolyte conductivity, $K_{\text{Cell}}$ is the cell constant, and $R_{\text{Elec}}$ is the electrolyte resistance which equals to the slope of V-I graph obtained from the LSV experiment. In this study, $K_{\text{Cell}}$ was quantified as 0.0333 cm⁻¹ utilizing a conductivity standard solution of $\delta_{\text{Elec}} = 1413$ μs.cm⁻¹.

Results and Discussion

Faradaic imbalance of the electrolyte over the long-term cycling impacts the discharge capacity of the flow cell substantially. Fig. 1 depicts the discharge capacity ratio to the theoretical capacity ratio for the flow cell with the electrolytes at different AOSs over 16 charge-discharge cycles at 200 mA.cm⁻² current density.

![Figure 1](image_url)

**Figure 1.** Discharge capacity to theoretical capacity ratio for the flow cells with the electrolytes at different AOSs over 16 charge-discharge cycles at 200 mA.cm⁻² current density.

will consequently result in better capacity retention for both 3.6+ and 3.7+ cases rather than ideally balanced case of 3.5+. This conclusion is reinforced by the moderate increase in coulombic efficiency which will be discussed below in the following paragraph. However, for AOS 3.8+, the discharge cycle is substantially limited by mass transport overpotential resulting in a significant capacity drop. Significant drop in the discharge capacity for high AOS values highlights the impact of faradaic imbalance on the flow cell performance. It also implies the necessity of implementing a smart monitoring system into the flow battery setup to detect the faradaic imbalance and alert the user before the system faces a complete failure which would be an important cost-saving step especially considering the long-term cycle life of the VRFBs. It is important to highlight that a very similar trend is observed for the charge capacity data.

Another way to assess the VRFB cell performance is to analyze the efficiency data which includes coulombic ($\eta_{\text{coul}}$), voltage ($\eta_{\text{v}}$), and energy efficiency ($\eta_{\text{E}}$). Fig. 2 demonstrates the efficiencies over 16 cycles for each AOS case. Based on the efficiency analysis, coulombic efficiency increases marginally with AOS increasing. This phenomenon can be explained by the increased amount of $V^{3+}$ ions in the higher AOS values; $V^{3+}$ has a lower diffusion coefficient compared to $V^{2+}$ across the membrane. Therefore, over cycling, crossover decreases for more imbalanced cases which consequently results in fewer self-discharge reactions and improved coulombic efficiency. With increasing AOS, voltage efficiency decreases due to the decrease in the amount of reactants required for charge-discharge process. This also causes an increase in activation overpotential in accordance with Butler-Volmer equation. While the average voltage efficiency is 72% for the ideally balanced case, it drops to 65% for the AOS 3.8+ case. Energy efficiency follows the same trend as voltage efficiency and decreases 6% between the best and worst cases. Since the efficiency values change marginally with AOS increasing, it is critical to confirm the reproducibility and accuracy of the data. To address this concern, the cycling experiment using the imbalanced case of AOS 3.6+ was repeated. The average deviation of the efficiency values compared with the first trial was found to be ±0.43, ±0.39 and ±0.82 for coulombic, voltage, and energy efficiency, respectively. This deviation proves the reproducibility of the data and makes the interpretation regarding the efficiency analysis reasonable.

In addition to studying the discharge capacity and efficiency values, both polarization curve and EIS measurements were also carried out to get a more clear understanding of the impact of faradaic imbalance on the flow battery performance. Fig. 3 shows both the polarization curves and power density measurements for each AOS case. As the AOS value increases, slope of the polarization curve which shows the ASR of the flow cell increases as well. Various phenomena can be responsible for the increased ASR value in imbalanced cases. First, lower conductivity and mobility of the imbalanced electrolytes can contribute to their increased ohmic resistance values. According to the literature, for same vanadium electrolyte composition, the conductivity of $V^{3+}$ ion is higher than $V^{5+}$, and the viscosity of $V^{2+}$ is higher than $V^{3+}$.[11,21,41] Accordingly, while the AOS increases the ratio of $V^{2+}$/V$^{3+}$ decreases which results in the decrease of the conductivity and mobility of the negative electrolyte. We also repeated the conductivity measurement experiment for all the electrolyte samples and the obtained data matches well with the trend in the literature.[21]

As depicted in Table II, the electrolyte conductivity decreases as the AOS value increases which is in a complete agreement with the

| Electrolyte Samples | Conductivity (mS.cm⁻¹) |
|---------------------|-----------------------|
| AOS 3.5+            | 192.4                 |
| AOS 3.6+            | 189.8                 |
| AOS 3.7+            | 185.9                 |
| AOS 3.8+            | 157.3                 |
| AOS 3.9+            | 144.3                 |

**Table II.** Conductivity values for different electrolyte samples.
Figure 2. a) Coulombic, b) voltage and c) energy efficiencies of the flow cells with the electrolytes at different AOSs at 200 mA.cm\(^{-2}\) current density.

The final step toward the evaluation of the performance of the cells is the EIS measurement which analyzes the contributions to the cell impedance and adds more detailed info to the polarization curve data. As shown in Fig. 4, high-frequency intercept which indicates the ohmic resistance of the cell shifts to higher values as the AOS increases. Cell ohmic resistance consists of an electronic contribution and an ionic contribution due to the membrane and electrolyte. The ionic resistance dominates the cell resistance due to the high conductivity of the other components. As discussed in the previous part, change in the electrolyte conductivity plus the change in the membrane conductivity can lead to a shift in the ionic resistance of the flow cell. Moreover, as the AOS increases, the first semicircle of the impedance curve gets larger indicating an increase in the charge transfer resistance (RCT). RCT results from charge transfer reactions at the interface between the electrode and electrolyte and different concentration of V\(^{2+}/V^{3+}\) ions may affect the kinetic overpotential of the cell. Similar to the first semicircle, the second one grows as well with increase in the AOS that depicts a higher mass transport limitation for the more unbalanced cases. As described before, deficiency of the ions and diffusion limitations contribute to the limit in mass transfer. Finally, the DC resistance which is indicated by the low-frequency intercept of the curve increases significantly with AOS increase as expected from the polarization curve. Although
Figure 3. (a) Polarization curve measurement (b) discharge power density curves for the flow cells with the electrolytes at different AOSs.

Figure 4. EIS measurements for the flow cells with the electrolytes at different AOSs obtained using the frequency range of 10 mHz to 100 kHz and implementing 5mV perturbation voltage.

increase in the imbalance ratio affects all three types of resistance in the flow battery, it has the most significant impact on the charge transfer resistance. In comparison to the ideally balanced case, $R_{ct}$ increases by 59% for AOS 3.6+ and this amount increases up to 709% for the worst case of 3.9+ (Table III). EIS measurement can also be used as a validation method for polarization curve data. As shown in Table IV, there is a good agreement between the polarization curve slope and the total DC resistance obtained through EIS. It is important to note that Kramers-Kronig compatibility test has been implemented for the EIS data reported. The normalized residual errors of the real and imaginary data of the EIS measurement were found to be 2.25% and 8.01%, respectively. Although not ideal, this satisfies a reasonable level of linearity for a quantitative comparison. The sources of non-linearity that are present in the system include the pulsation from peristaltic pump and variation in the local state of charge (i.e., the state of charge in the flow cell) especially during the low frequency measurements.

It is clear from all the obtained results that a shift of AOS from the ideal value of 3.5+ has a negative impact on all aspects of the system performance. Hence, during long-term cycling operation, if the cause of the faradaic imbalance (e.g. side reactions) is not addressed, the system performance will eventually suffer from significant degradation. Moreover, it is important to note that this work investigates specific AOS conditions – the rate of AOS shift directly depends on the rate of the parasitic side reactions. However, the concentration of other species in the electrolyte ($H^+, HSO_4^-, SO_4^{2-}$) may also change depending on the side reactions present in the system. For instance, $H_2$ evolution will cause the pH of the electrolyte to rise and with an increase in $pH$, deprotonation increases and the stability of the $V^{5+}$ decreases. This will eventually cause $V^{5+}$ to precipitate. Another contribution of pH to the flow cell performance is its impact on the positive side reaction kinetics. In comparison with the negative electrode, the positive redox couple sustains a relatively slow dynamic reaction, due to the rearrangement of the coordination structures of the vanadium ions which consists in the transfer of electrons, the exchange of protons, and the formation of a number of intermediate complexes. Electrolyte pH is one of the major factors affecting these rearrangements resulting in a significant change in the flow cell performance.

The magnitude of these secondary effects depends on the specific sources of faradaic imbalance. Additionally, due to the oxygen including functional groups in sulfuric acid solution, electrode surface activation level changes for different acid concentrations. As a result, electrochemical characterization of electrolytes which have different concentrations of vanadium ions and sulfuric acid can provide insightful information for the performance of VRFB.

Conclusions

In VRFBs parasitic side reactions such as gas evolution occurring in both half-cells of the flow cell cause faradaic imbalance, which is a shift in the AOS of the electrolyte. Unlike stoichiometric imbalance, this kind of imbalance cannot be corrected through electrolyte remixing processes and requires chemical or electrochemical treatment to balance the AOS through input/output charged species. In this study, we investigate the performance degradation of the flow cell utilizing electrolytes with different AOS values. Based on the obtained data, it is observed that discharge capacity, coulombic/voltage efficiency, and power characteristics all decrease as AOS shifts from the ideal case of 3.5+. Furthermore, increase in the AOS value substantially impacts all the ohmic, charge transfer, and mass transfer resistances. For AOS 3.9+ case, a 19.3%, 709%, and 206% increase is observed in ohmic, charge transfer, and mass transfer resistances respectively. Moreover, for the same electrolyte sample, available power density drops more than 40% in comparison with the balanced case of 3.5+ and discharge capacity depicts 52% drop from the theoretical limit. This huge performance degradation is related to the deficiency of the charged ions due to self-discharge and other parasitic side reactions. Performance degradation of the flow cell utilizing electrolyte samples with higher AOS values can be attributed to various electrolyte characteristics, such as conductivity, ion mobility, concentration, and viscosity).
As reported in this study, faradaic imbalance has a severe negative impact on the flow cell performance, and over long-term cycling it will get even more concerning. This performance degradation is likely to become apparent during the long lifetime of a commercial VRFB and should be considered to prevent the flow cell failure. Periodic maintenance may be required to correct the imbalance and maintain the acceptable performance of the battery. In addition to experimental characterization of the effects of faradaic imbalance, numerical simulations to model the side reactions which give rise to this issue should also be developed. Conducting both experimental and numerical approach will help us to further understand the nature, causes, and impacts of faradaic imbalance resulting in proposing mitigation techniques to avoid the possible cell failure over the long-term performance of a VRFB.

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### Table III. Ohmic, charge transfer, and mass transfer resistances including their increase rate with respect to AOS 3.5+ for the flow cells with the electrolytes at different AOSs.

| AOS | \( R_Ω (\Omega \cdot cm^2) \) | Increase Rate of \( R_Ω \) (%) | \( R_{CT} (\Omega \cdot cm^2) \) | Increase Rate of \( R_{CT} \) (%) | \( R_{MT} (\Omega \cdot cm^2) \) | Increase Rate of \( R_{MT} \) (%) |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 3.5+ | 0.507 | - | 0.098 | - | 0.213 | - |
| 3.6+ | 0.543 | 7.1 | 0.155 | 58.2 | 0.231 | 8.5 |
| 3.7+ | 0.544 | 7.3 | 0.224 | 128.6 | 0.292 | 37.1 |
| 3.8+ | 0.604 | 19.1 | 0.487 | 396.8 | 0.357 | 67.6 |
| 3.9+ | 0.605 | 19.3 | 0.793 | 709.2 | 0.653 | 206.6 |

\( R_Ω \) Ohmic resistance.
\( R_{CT} \) Charge transfer resistance.
\( R_{MT} \) Mass transfer resistance.

### Table IV. Comparison between the total DC resistance of the flow cells with the electrolytes at different AOSs obtained through polarization curve and EIS measurement.

| AOS | Polarization Curve \( (\Omega \cdot cm^2) \) Increase Rate of \( R_Ω \) (%) | EIS \( (\Omega \cdot cm^2) \) |
|-----|-----------------|-----------------|
| 3.5+ | 0.83 | 0.82 |
| 3.6+ | 0.95 | 0.93 |
| 3.7+ | 1.18 | 1.06 |
| 3.8+ | 1.44 | 1.45 |
| 3.9+ | 2.43 | 2.41 |
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