DESIGN, CONSTRUCTION, AND STUDY OF PERFORMANCE IMPROVEMENT IN A VANADIUM REDOX FLOW BATTERY

A Thesis in
Mechanical Engineering

by
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ABSTRACT

A reliable Vanadium Redox Flow Battery (VRB) system was designed, built, and tested in a laboratory environment. Properties of components assembled inside a cell determined the polarization losses and consequently the performance of the VRB. As part of the research, the impact of the graphite felt electrode and a turbulent promoter placed between the electrode and the membrane were investigated. For the graphite felt electrode, a thermal pretreatment significantly enhance the performance of a VRB. The turbulent promoter was designed to promote the diffusion rates of active species from the reaction surface in the electrode to the membrane. The water transport through the polymer membrane, which changes the concentration of electrolytes and has a deterministic role in performance, was also measured in the study. The open circuit voltage of self-discharge was recorded for monitoring crossover through the polymer membrane.

The energy efficiency of the VRB was 77\% by using the thermal pretreatment graphite felt at 400\°C for 30 hours, which is 29\% higher than the VRB using the non-treatment graphite felt under the same test conditions. The usage of the turbulent mesh slightly enhanced the Coulombic efficiency, however the energy efficiency slightly decreased. Approximately 15\% amount of water transported through the membrane from the negative to the positive half cell after 14 hours charge-discharge operation. During the self-discharge process, the Nafion 117 took 90 hours for OCV to reduce to 0.2 V after charged state at 90\% state of charge SOC. The results in this study can help 1-D and 2-D modeling of the fluid mechanism inside a VRB cell design enhanced internal architectures to minimize ohmic losses.
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NOMENCLATURE

Acronyms

RFB         Redox Flow Battery
VRB         Vanadium Redox Flow Battery
SEI         Sumitomo Electric Industries
PTFE        Polytetrafluoroethylene
PVDF        Polyvinylidene
PSB         Sodium Polysulfide/Bromine Redox Flow Battery
PAN         Polyacrylonitrile
SOC         State of Charge
STP         Standard Conditions for Temperature and Pressure
RDE         Rotating Disk Electrode
SHE         Standard Hydrogen Electrode
EE          Energy Efficiency
CE          Coulombic Efficiency
VE          Voltage Efficiency
ICV         Initial Charge Voltage
IDCV        Initial Discharge Voltage
DI Water     Distilled Water
Re          Reynolds Number
OCV         Open Circuit Voltage

Parameters

M = Molar concentration (mole/L)
Q = Electrolyte flow rate (mL/min)
\( E^\Phi \) = Standard potential of overall Vanadium Redox Flow Battery cell (V) 
\( E^\Phi \) = Standard potential (V) 
\( E \) = Equilibrium voltage (V) 
\( E_{\text{bulk}} \) = Voltage in bulk solution (V) 
\( E_S \) = Voltage at the surface of electrode (V) 
\( R \) = Gas constant (8.3144 J/K/mol) 
\( T \) = Temperature (K) 
\( F \) = Faraday’s constant (96485 C/mol) 
\( C_i \) = Concentration of the different vanadium ions (mole/L) 
\( C_{\text{cell}} \) = The average cell concentration of different vanadium ions (mole/L) 
\( E_{\text{loss}} \) = Total loss inside VRBs (V) 
\( E_{R\text{-loss}} \) = IR loss inside VRBs (V) 
\( E_{\text{cell}} \) = The cell voltage (V) 
\( R_{\text{eq}} \) = Equivalent resistance (\( \Omega \)) 
\( t \) = Time (s) 
\( i \) = Current (A) 
\( i_o \) = Exchange current (A) 
\( n \) = Number of moles of electrons exchange in a reaction (N) 
\( P \) = Pressure (Pa) 
\( P_a \) = Ambient temperature (Pa) 
\( P_h \) = Maximum temperature of tank (Pa) 
\( N_{\text{cycles}} \) = The number of nitrogen injecting cycles (N) 
\( V \) = Electrolyte volume (m\(^3\)) 
\( N_{\text{cell}} \) = The number of VRB cell (N) 
\( b \) = The negative or positive sign (if the vanadium ions decrease, the sign is negative sign; if the vanadium ions increase, the sign is positive)
Greek Letters

$\eta_{\text{eq}}$ = Equivalent Overpotential

$\eta_{\text{act}}$ = Activation Overpotential

$\eta_{\text{conc}}$ = Concentration Overpotential

$\alpha$ = Charge Transfer Coefficient

$\eta_{V}$ = Voltage Efficiency

$\gamma_{i}$ = Activity Coefficient
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Chapter 1

Introduction

1.1 General Redox Flow Battery Background

In the 1970s NASA studied the Redox Flow Battery (RFB) for building stationary energy storage systems. In early 1984 Maria Skyllas-Kazacos and co-workers at the University of New South Wales, Australia developed the first Vanadium Redox Flow Battery (VRB). In 1998 the Australian Pinnacle Vanadium Redox Batteries Company bought the basic patents, and later Sumitomo Electric Industries (SEI) designed cell stacks and completed integrated systems under a license from Pinnacle VRB Company (S. Eckroad, 2007). Among various kinds of RFBs, the Vanadium Redox Flow Battery (VRB) was the first one introduced into commercial energy storage applications by SEI in 1996. In 1996, Kashima Kita Power Station utilized an in-load leveling application with 800kWh. Between 1996 and 2005, SEI had built VRB plants for solar energy storage (240kWh), wind turbine output stabilization and storage (6MWh), power quality (1500kWh), and peak shaving (5MWh) (S. Eckroad, 2007).

There are several characteristics that all RFBs share that make them attractive options for many energy storage applications. The oxidation and reduction reactions happen between two electrolytes, rather than between electrolyte and electrode inside the flow battery cell. Therefore, there is no electro-deposition or loss of electro-active substances. Also, electrolytes are stored in external storage tanks and are circulated through the cell stack by a pumping loop (Christian BLANC, 2009). However, the most significant characteristic of RFBs is that the power and energy capacities are independent. In a flow battery system, power is determined by both the rate of reaction at each electrode and the total surface area of the electrodes, whereas
energy is determined by the storage capacity and concentration of the electrolytes (M. Gattrell et al., 2004). Since the cells of VRBs are easily stacked in parallel or series, increasing the power output or voltage is simplified. Additionally, by increasing the volume of the electrolytes in external storage tanks, energy capacity can be scaled up (C. Ponce de Leon et al., 2006). The advantage of scaling up easily with an energy scale from 10kW to 10MW makes RFBs attractive candidates for large stationary storage applications (Electricity Storage Association, 2010).

There are many common advantages among different types of RFBs, such as Vanadium Redox Flow Battery, Iron-Chromium Redox System, Zinc/Bromine Redox Flow Battery, and Zinc/Cerium Redox Flow battery, etc. The flow battery systems have long life cycles (10,000-16,000 cycles) and low specific costs (100-1000 $/kWh) (Electricity Storage Association, 2010). They require low maintenance and are tolerant to deep discharges (97.5% state of charge SOC) without any risk of damage. The net efficiency of flow battery systems can attain 85%, and response time is as rapid as 350 µs. The operation temperature of RFBs ranges from 10°C to 40°C (Electricity Storage Association, 2010). Finally and very importantly, flow battery plants are also geographically independent, which compares favorable to many other energy storage systems, such as pumped hydro.

Currently, flow battery systems have several technical barriers limiting their development. The main problem is their low energy density (15-70 Wh/L and 15-50Wh/kg), which is five to ten times lower than the lithium-ion battery, which is usually applied on mobile systems (Maria Skyllas-Kazacos et al., 2010). The low energy density in RFBs is due to the limited solubility of active materials in electrolytes, which also limits the operating temperature (Maria Skyllas-Kazacos, 2010). Another problem is the cross-contamination of active ions and water molecules through the ion conductive membranes, causing unwanted changes in concentrations.
and species in electrolytes (C. Ponce de Leon et al., 2006). Recently, more research
groups are studying flow battery systems. RFBs are environmental friendly and with
high-energy efficiency output. Since the limited availability and increasing cost of
petroleum continues, the demand of green energy, such as solar and wind energy, has
been increasing. RFBs are also candidates as large energy storage systems coupled
with these renewable but intermittent renewable sources to provide grid-based energy
storage. If the power density of RFBs could be further improved, they would have
potential to be utilized in mobile systems as well.

The vanadium redox flow battery is one of the most attractive flow battery
systems, and has already been applied to commercial energy storage applications.
VRBs are generally intended for storage applications from 2.5kW to 10MWs with
durations of two hours or more (Electricity Storage Association, 2010). The
prominent advantage of VRBs is that they utilize vanadium ions in both positive and
negative electrolytes, so the cross-contamination of active ions across membrane can
be reduced (C. Ponce de Leon et al., 2006). Additionally, no toxic production occurs
during VRBs operation, whereas toxic Br\textsubscript{2} gas is produced during the operation of the
Zinc/Bromine Redox Flow Battery (C. Ponce de Leon et al., 2006). Although the
specific cost of VRBs is lower than other RFB systems, the price of raw material of
vanadium electrolyte V\textsubscript{2}SO\textsubscript{4} is over half the cost of the whole VRB system, which
presents a major limitation. Unfortunately, vanadium is also used in the production of
steel and its price is likely to follow the rise of the raw material market (Christian
BLANC, 2009).

The VRB system is not only the most researched flow battery system, but it
is also the most promising storage system for large energy systems, and are the main
focus of this study.
1.2 VRB Operation

Figure 1.1 is a simple schematic of a VRB system during the charge and discharge processes. In both charge/discharge processes, we define the VO\textsuperscript{2+/3+} couple as positive, whereas define the V\textsuperscript{2+/3+} couple as negative for convenient explanation in the following sections. The reactions of VRBs at the anode and cathode are shown below in Eq. 1.1. Nitrogen gas is usually supplied, having it circulate through the negative storage loop to prevent V\textsuperscript{2+} from reacting with oxygen. Ideally, there is no consumption of electrolytes during the charge-discharge operation of the system. However, complicated side reactions can consume electrolytes and change the concentration of electrolytes during its system operation. Eq. 1.2 shows side reactions of H\textsubscript{2} and O\textsubscript{2} produced from water molecules.

\begin{align*}
\textit{Positive half cell:} & \quad \text{Charge} \\
& \quad \text{VO}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{VO}_2^{+} + 2\text{H}^+ + e^- \\
\text{Discharge} \\
\textit{Negative half cell:} & \quad \text{Charge} \\
& \quad \text{V}^{3+} + e^- \rightleftharpoons \text{V}^{2+} \\
& \quad \text{Discharge}
\end{align*}
Figure 1.1: Vanadium redox flow battery schematic (not to scale).
**Hydrogen evolution:** \[2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-\]

**Oxygen evolution:** \[2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^- + 4\text{H}^+\]

During the charge process, \(\text{H}^+\) ions are transported through an ion conductive membrane separated the electrolyte solutions from a positive half-cell to a negative half-cell, while electrons are externally supplied. During the discharge process, \(\text{H}^+\) ions are transported through a membrane from a negative half-cell to a positive half-cell, while electrons are inhibited by the non-electron conductive polymer membrane and must travel through the bipolar plate and externally through the load to a return cathode. Electrolytes in both external storage tanks circulate through the cell by a pumping loop, refreshing active ions to the positive and negative half-cells until the desired state is achieved.

Stability and concentration of vanadium ions in sulfuric acid are essential for VRBs. All VRBs employ \(\text{VO}^{2+}/\text{VO}_2^+\) (\(\text{V}^{4+}/\text{V}^{5+}\)) as the positive electrolyte and \(\text{V}^{2+}/\text{V}^{3+}\) as the negative electrolyte. Usually, the electrolyte consists of 1-2 M vanadium ions in 2 M sulfuric acid solutions, which serves as a supporting electrolyte (Erik Kjeang et al., 2007). One possibility to improve the energy density of VRBs is to increase the vanadium concentration. However, Faizur Rahman et al. pointed out that a vanadium ion concentration above 2M in the sulfuric acid supporting electrolyte leads to super-saturation of the solution, resulting in the precipitation of the electrolyte at low temperatures in the case of \(\text{V}^{2+}/\text{V}^{3+}\) or \(\text{V}^{4+}\) solutions, or at elevated temperatures in the case of a \(\text{V}^{5+}\) solution (Faizur Rahman et al., 2009). Therefore, an important issue is to research how to improve the stability of vanadium ions while increasing vanadium concentrations.

The general membrane separator used in VRB is an ion conductive
membrane. The most common membranes are Nafion® membranes 115 and 117, with an approximate dry thickness of 51 to 175 microns (Larminie and Dicks, 2003). During the charge-discharge operation and self-discharge operation, vanadium active ions and water molecules crossing through the membrane change the concentration of electrolytes. Many studies have attempted to modify the polymer membrane to reduce cross-contamination. Jingyu Xi et al. modified the Nafion membrane with SiO₂ in an attempt to reduce the crossover of the vanadium ions and water molecules through the membrane. The self-discharge time increased significantly, and the crossover problem was reduced. Figure 1.2 demonstrates the procedure of membrane modification and the differences in permeability of different vanadium ions between Nafion and Nafion/SiO₂ hybrid membranes (Jingyu Xi et al., 2007)

Figure 1.2: Nafion/SiO₂ hybrid membrane. (a) Schematic depiction of the preparation of Nafion/SiO₂ hybrid membrane. (b) Top: Schematic illustration of the cell for the measurement of vanadium permeability; Bottom: Comparison of the permeability of vanadium ions through the membrane between Nafion and Nafion/SiO₂ hybrid membrane. From Jingyu Xi et al., 2007.
Figure 1.3 is a schematic of structure of a VRB cell. On each side of the membrane are flow frames (1-3 mm thick) for electrolytes to flow directly through the graphite-felt electrodes. The flow rate of the electrolytes influences the reaction rate of the vanadium ions on the electrode surface. Under the diffusion control condition, if the flow rates of the electrolytes increase, then the reaction rate of vanadium ions will increase and the Coulombic efficiency of the VRBs will subsequently increase. Besides, high flow rate can reduce the rates of hydrogen and oxygen evolution. A.A. Shah et al. made the conclusion that the relative gain in Coulombic efficiency decreases as the flow rate is increased, which in turn suggests that there is a flow rate of optimum performance versus the volumetric flow by the experimental results (A.A. Shah et al., 2008).
The thickness of the flow frame is around 1mm-3mm, and the electrolyte flows through the electrode is normally laminar based on Reynolds number calculation. For promoting the diffusion rate of charge species from the reactive surface in the carbon electrode to the membrane, a thin turbulent mesh (around 0.5mm) can be placed inside the flow frame. For the vanadium flow battery system, the basis of the vanadium electrolyte in both half-cells is 1M – 4M of sulfuric acid solutions, so the materials for the flow frame used inside the VRBs is polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) for the turbulent mesh, which is acid resistant to acid solutions (M. Kazacos et al., 1990).

The graphite felt or the carbon felt electrode is placed inside the flow frame and combined with a graphite bipolar plate. The properties of a graphite felt electrode control the activation kinetic in VRBs. Usually, polyacrylonitrile- (PAN) based graphite or carbon felt is used as the electrode for VRBs because of their wide operation potential range, their stability as both anode and cathode, and their availability in high surfaces areas at reasonable costs (H. Kaneko et al., 1991). Thermal treatment for graphite or carbon electrodes has been indicated to significantly improve kinetic reversibility of PAN graphite felt and reduce activation loss (M. Rychcik et al., 1987). Modifying the graphite felt with catalyst is another method to enhance the kinetic reactions on the graphite felt electrode. Hantao Zhou et al. improved the energy efficiency of the sodium polysulfide/bromine flow battery (PSB) to approximately 20% higher by catalyst-coating carbon felt with Na$_2$S$_x$ compared with using raw carbon felt (Hantao Zhou et al., 2006). Although the kinetics of graphite felt inside VRBs are different from PSBs, the catalyst-coating carbon felt electrode may also improve the performance of VRBs. Figure 1.4 shows the microscope images of fibers of pure graphite felt and Co loaded graphite felt. The graphite felt electrode is combined with a graphite bipolar plate working as the
current collector, providing electrical contacts for the load.

Figure 1.4: Microscope images of fibers of: (a, c) pure graphite felt; (b, d) Co loaded graphite felt. (a, b) 1000x; (c, d) 500x. From Hantao Zhou et al., 2006.

The standard thermodynamic open circuit voltage of the flow battery cell can be calculated by using thermodynamic equation Eq. 1.3, which shows the standard potential for the cathode and anode of a VRB. The potential for an overall VRB cell ($E^\Phi$) is 1.255V at standard conditions for temperature and pressure (STP). From the Nernst equation, equilibrium voltage (E) of a VRB cell is determined as Eq. 1.4 under the condition that set the product/ ratio of the activity coefficient ($\gamma_i$) to be 1 (A. Heintz et al., 1998).
A charge-discharge plot under constant current density is usual to quantify the performance of VRBs. Figure 1.5 shows three stages in a charge-discharge plot at a constant current density of 60mA/cm$^2$. Stage A represents the stage at the beginning of charge and discharge, which is dominated by activation and ohmic losses inside the cell. The cell with lower losses has a lower initial charge voltage and a higher initial discharge voltage (Ping Zhao et al., 2005). In Stage B, the voltage sharply changes in the end of charge and discharge processes, due to the mass transport limitation. Voltage changes smoothly in Stage C. More, concentrations of vanadium species in electrolytes are the factors that dominate the rates of voltage changes in the cell in Stage C (Peng Qian et al., 2008). The charge and discharge current density also determines the rate of voltage change. The cell applied with a lower current density has a lower rate of voltage change and higher energy efficiencies (Peng Qian et al., 2008).

\[
\begin{align*}
V^{3+} + e^- & \rightleftharpoons V^{2+} & \phi_{\text{anode}} = -0.255 \text{ V} \\
VO_2^+ + 2H^+ + e^- & \rightleftharpoons VO^2+ & \phi_{\text{cathode}} = 1.000 \text{ V} \\
E^\Phi = \phi_{\text{anode}} - \phi_{\text{cathode}} & = 1.255 \text{ V} \\
E = \phi^\Phi + \frac{RT}{F} \ln \left[ \frac{\text{CVO}_2^+ \times C^2H^+}{\text{CVO}^{2+}} \right]_{\text{catholyte}} \left( \frac{\text{CV}^{2+}}{\text{CV}^{3+}} \right)_{\text{anolyte}} \quad \text{[V] 1.3}
\end{align*}
\]
1.3 Internal Losses of VRBs

Definition and techniques of measuring losses are essential for analyzing the performance and qualities of all components used inside the flow battery cell. There are four main losses inside the cell: activation overpotential, concentration overpotential, IR loss, and self-discharge crossover. Generally, activation and ohmic losses dominate in the VRB cell (Ping Zhao et al., 2005). Figure 1.6 shows total losses of the system found from the polarization curve (M. Skyllas-Kazacos et al., 1997). Charge equivalent overpotential $\eta_{\text{eq,charge}}$ combines activation overpotential and mass transport overpotential, and the same technique as discharge equivalent overpotential $\eta_{\text{eq,discharge}}$ Eq. 1.5 shows the definition of total loss $E_{\text{loss}}$, i.e. the difference between the equilibrium voltage $E$ and the cell voltage $E_{\text{cell}}$, during the
charge and discharge processes (M.-H. Li et al., 2007). The equivalent resistance for 19 VRB cells is shown in Figure 1.6. The OCV of the cell is the equivalent voltage while there is no current through the cell. However, the cell voltage will change immediately when current is applied or withdrawn from the cell, as shown in Eq. 1.6 (J. Van herle, 2002). Therefore, the cell with lower losses has both a lower charge voltage and a higher discharge voltage, with subsequently higher efficiencies.

\[
E_{\text{loss}(t)_{\text{charge/discharge}}} = R_{\text{eq,charge/dischage}} \left| i(t) \right| + \eta_{\text{eq,charge/dischage}} \quad [V] \quad 1.5
\]

Figure 1.6: Polarization curves at approximately 50% state of charge SOC for 19 cell stacks. The open circuit voltage OCV is 26.3V. From Christian Blanc, 2009. Experimental Data are from M. Skyllas-Kazacos et al., 1997.

\[
E_{\text{cell,discharge}} = E - E_{\text{loss,discharge}}
\]

\[
E_{\text{cell,charge}} = E + E_{\text{loss,charge}} \quad 1.6
\]
1.3.1 Activation Overpotential

The activation overpotential (activation loss) is due to electrochemical kinetics on the electrodes. It is associated with energy required to initiate a charge transfer between reactants and electrodes (Christian BLANC, 2009). The rate of the reaction determines the magnitude of the activation overpotential, so a slower reaction requires a larger overpotential than a faster reaction. In the VRB system, activation overpotential $\eta_{act}$ could be calculated by applying the Butler-Volmer equation as Eq. 1.7 (Christian BLANC, 2009).

$$\eta_{act} = \frac{RT}{\alpha n F} \ln(i) - \frac{RT}{\alpha n F} \ln(i_o)$$

$\alpha$ is charge transfer coefficient; $i$ is applied current; $i_o$ is exchange current; $n$ is number of moles of electrons exchange in the rate limiting charge transfer reaction. The symmetry factor is also called charge transfer coefficient (dimensionless) in electrode kinetic (M. Gattrell et al., 2005).

The typical technique to measure overpotential on electrodes is an $i$-$V$ polarization curve. A rotating disc electrode RDE is used with a reference of a standard potential electrode, such as a standard hydrogen electrode SHE. Figure 1.5 shows the overpotential plot of $VO^{2+/V^{2+}}$ ($V^{4+/V^{5+}}$) and $V^{2+/V^{3+}}$ couples during charge and discharge (M. Gattrell et al., 2004). In VRBs, the kinetics of the $V^{2+/V^{3+}}$ couple is faster than the $VO^{2+/V^{2+}}$ couple, and the kinetics on the charge process are faster than the discharge process. This means a larger overpotential is necessary to initiate the charge transfer on the anode in the VRB system (Christian Blanc, 2009). M. Gattrell et al. pointed out that the reason for a low apparent transfer coefficient for the reduction of $VO^{2+}$ might be that the electron transfer to the reaction species
through a layer of adsorbed intermediates of that layer are slow to desorb from the electrode surface. Therefore, the entire applied potential is not available to drive the rate-determining step, leading to the observed, low apparent symmetry factor.

Figure 1.7: Graphite RDE, 4000 rpm, 0.1 mV/s, 1 M H$_2$SO$_4$, 20°C. For V$^{2+}$/V$^{3+}$, ca. 16 and 36 mM V$^{3+}$. For VO$^{2+}$/VO$_2^+$ (V$^{4+}$/V$^{5+}$) 31 mMVO$^{2+}$, and 19 mM VO$_2^+$. From M. Gattrell et al., 2004.

Since activation loss is important, many studies have attempted to improve the dynamic reaction of the cell, such as utilizing the thicker graphite felt electrode on a VO$^{2+}$/VO$_2^+$ half-cell. As mentioned before, thermal treatment on the graphite felt electrode could significantly improve the kinetics of the graphite electrode. The reason might be that oxygen groups introduced by thermal treatment on the electrode surface probably functioned as active sites, making oxygen transfer from oxygen groups easier than directly from H$_2$O (B.E. Conway et al., 2002). Thermal treatment also could increase its crystallinity and conductivity (M. Shimada et al., 1985). W.H. Wang et al. proved that Ir-modified carbon felt could decrease 25% of the cell
resistance compared to the cell using non-modified felt (W.H. Wang et al., 2007).

1.3.2 Concentration Overpotential

Since the vanadium concentration of a bulk solution is different from the concentration on the electrode surface, this difference leads to a mass transport overpotential. In electrochemical systems, reactive ions diffuse from the diffusion layer to an electrode surface, and electron transfers happen only within the thin reaction layer (< 1nm) of a solution immediately adjacent to the surface of the electrode (Christian BLANC, 2009). When the moving rate of a reactant species is slower than the electrochemical reaction rate and the leaving rate of a product species is slower, then the mass transport overpotential is triggered (Christian BLANC, 2009). Figure 1.8 shows the concentration changes in the electrolyte with the different layers. The transport of the reactant and the products is mainly driven by three mechanisms: diffusion, migration, and convection. Eq. 1.8 is the equation to calculate mass transport overpotential in VRBs (F. Grasser, 2005).

\[ \eta_{\text{conc}} = E_{\text{bulk}} - E_S = \]

\[ \frac{RT}{F} \ln \left\{ \frac{CVO_2^+(\infty)C^2H^+(\infty)CV^2+(\infty)}{CVO^2+(\infty)CV^3+(\infty)} \ast \frac{CVO^2+(0)CV^3+(0)}{CVO_2^+(0)C^2H^+(0)CV^2+(0)} \right\} \]
Figure 1.8: Concentration changes in different layers of electrolyte. (not to scale) From Christian BLANC, 2009.

Measuring concentration overpotential is difficult, since it is not easy to measure the vanadium concentration on the electrode surface. Many factors influence the concentration overpotential of the cell, such as concentration, viscosity, and flow rate of electrolytes flowing through the cell. Electrolyte viscosity increases while electrolyte concentration increases, and therefore concentration loss increases. The cell with a higher flow rate has more evenly distributed concentration overpotential and transfer current density in the porous electrode, and leads to a higher Coulombic efficiency and lower rates of hydrogen and oxygen evolution (A.A. Shah et al., 2008).

1.3.3 IR Loss

In the VRB system, IR loss is contributed by both ohmic and ionic losses.

Ohmic loss is due to electron conduction in the graphite felt electrodes, graphite bipolar plates, current collector, and contact loss between electrodes and bipolar plates. The thermal bonding technique or novel electrode-bipolar assembly could reduce
contact resistance, between the electrode and the bipolar plate, which is significantly important (Peng Qian et al., 2008). Ionic loss is due to ionic conduction in the electrolytes and the membrane (Christian BLANC, 2009). Figure 1.9 shows a schematics of the total IR loss schematic inside the half-cell of a single VRB cell. The properties of all components inside the cell influence the IR loss. Membrane ohmic loss and electrolyte ionic loss are dominant factors of total IR loss. All resistance from IR loss could be represented by $R_{eq,charge/discharge}$. Eq. 1.9 shows the IR loss voltage.

![Figure 1.9: All IR loss components inside the flow battery cell.](image)

$$E_{R\cdot\text{loss}(t)\text{charge/discharge}} = R_{eq,\text{charge/discharge}} \cdot |i(t)|$$  

1.9

It is obvious from Eq. 1.9 that the IR loss will increase if the applied current for the flow battery system increases. The charge voltage will be higher and the discharge voltage will be lower if the loss of the cell increases. Then the side reactions will happen more readily at a higher operation voltage. Also, the concentration gradient will increase while the overpotential, transfer current densities, and the applied current density increase. In this case, the higher concentration polarization occurs inside the porous electrodes (Dongjiang You et al., 2009).
1.3.4 Other Losses of VRBs

During cell operation, cross-contamination problems of active vanadium species, water molecules and side reactions cause losses of VRBs. Figure 1.10 shows that the mechanisms of vanadium ions and water molecules crossover through the Nafion membrane during charge-discharge cycles and also during the self-discharge of cells (C. Sun et al., 2010). Different concentrations of vanadium ions in positive and negative half-cells result in vanadium species crossover through the membrane separator. Different vanadium ions have different diffusion coefficients through different kinds of membranes, as shown in Table 1.1. Since $V^{2+}$ easily oxidizes in air, the study did not measure the permeability for $V^{2+}$ ions. Vanadium ions also drag water molecules during crossover through the membrane, and proton ions also drag water molecules transferring through the membrane from the opposite direction for charge balance, during both the charge-discharge cycles and self-discharge cycles. During charge-discharge cycles, there is additional proton ion transfer through the membrane for the formation of the internal electric circuit in solution. Additionally, osmosis is the main force driving 75% of the water molecules transferring through the membrane (Chenxi Sun et al., 2010).

| Table 1.1 : Diffusion coefficients of vanadium ions. From Xuanli Luo et al., 2005 and Chenxi Sun et al., 2010. |
|---|---|---|---|---|
| | $V^{2+}$ | $V^{3+}$ | $VO^{2+}$ | $VO_2^+$ |
| Nafion 117 | 5.261 | 1.933 | 4.095 | 3.538 |
| Diffusion coefficient $\times 10^3$ cm$^2$ min$^{-1}$ | 3.655 | 3 | 7.02 |

(From Xuanli Luo et al., 2005)

(From Chenxi Sun et al., 2010)
Side reactions consume electrolyte, current and impact efficiencies of the flow battery. Oxygen and hydrogen evolutions from water molecules are two essential side reactions in VRBs. In order to drive the H$_2$ reaction, partial consumption of the
applied current occurs on the cathode, whereas partial consumption by $O^2$ reaction occurs on the anode during the charge process (A.A. Shah et al., 2010). When side reactions happen, the gas bubbles with a diameter of 25µm–100µm form on the surface of the electrodes, and then reduce the effective reactions areas on the electrodes. H. Al-Fetlawi et al. estimated that the $O^2$ gas volume is approximately 2~13% of the total volume during typical charge-discharge cycles, and $O^2$ evolution dropped its charge efficiency by 5-10% through simulation (H. Al-Fetlawi et al., 2010). Side reactions in vanadium electrolytes are extremely complicated. There are many kinds of vanadium species, such as HVO$_3$ and H$_2$VO$_4^-$, which also exist in vanadium electrolytes and will react with water molecules and other vanadium species (Ch. Fabjan et al., 2001).

The motivation of this work is to develop VRB systems which offer promise on grid-level storage of energy. The specific objectives are as follows:

1) To develop a flow battery testing system for use in the lab.

2) To demonstrate repeatable performance using this test system.

3) To investigate the internal losses of the VRB system, and evaluate the effectiveness of the use of a turbulent mesh for promotion of ionic charge transport in the electrolyte, and the thermal pretreatment of the electrode for promotion of the kinetics.
2.1 The Preparation of Vanadium Electrolyte

Vanadium (IV) sulfate oxide hydrate, 99.9% (metal basis), VOSO$_4 \cdot 3.7$H$_2$O, is the raw material of vanadium electrolytes in both positive and negative half-cells (Alfa Aesar ®). The supporting electrolyte is prepared from a concentrated sulfuric acid solution, 96% by weight (EMD CHEMICALS). The 2M supporting sulfuric acid solution was prepared with DI water. To prepare the solutions, prepare 1.67M vanadium electrolyte in the 2M supporting sulfuric acid solution. The vanadium electrolyte is then placed in a sonication machine at 80°C until the VOSO$_4$ vanadium powder is fully dissolved, and appears as a clear blue VO$^{2+}$ color (Erik Kjeang et al., 2007).

The VO$^{2+}$ vanadium electrolyte is then stored in positive and negative external storage tanks with the proportion of volume of 2:1. The electrolyte is circulated through the cell and the cell is charged with a constant current density of 60mA/cm$^2$. Eq. 2.1 shows the reactions of the original 1.67M VO$^{2+}$ electrolyte at anode and cathode during the charging of the cell. The cell is continuously charged until the cell until reaches its fully charged state, 2V, confirmed by the color change of electrolytes. During the charge process, the vanadium electrolyte color changes from blue VO$^{2+}$ ($V^{4+}$) to green $V^{3+}$ and to purple $V^{2+}$ at the cathode. At the anode, the electrolyte color changes from blue VO$^{2+}$ ($V^{4+}$) to yellow VO$_2^+$ ($V^{5+}$). Figure 2.1 shows the various colors of different vanadium ions. The equipment to provide current and load for the cell is a multi-channel battery testing system, BT2000 (Arbin Instruments Corp., USA). The Arbin Battery Testing System also measures and records voltage, operating time, power, and current capacity through Arbin MITS Pro.
After the cell attains its fully charged state, half the volume of the VO$_2^+$ (V$^{5+}$) vanadium electrolyte is extracted from the positive tank, and the cell is discharged with the same current density as the charge phase, 60mA/cm$^2$ until the cell voltage reaches 0.8V (Erik Kjeang et al., 2007). As the result, the blue VO$_2^+$ and green V$^{3+}$ vanadium electrolytes are produced at the positive and negative storage tanks, respectively. Eq. 2.2 shows the reactions of the cell during discharge. During the operation of the cell, nitrogen gas is continuously injected into negative and positive electrolyte loops for preventing vanadium ions reaction with oxygen, and pressure P maintains 5 psi at both positive and negative storage tanks.
Cathode \[ V^{5+} + e^- \rightarrow V^{4+} \]
Anode \[ V^{2+} \rightarrow e^- + V^{3+} \]

It is worth mentioning that a red thermal precipitate, \( V_2O_5 \) polymer, is formed hydrothermally in the fully charged positive half-cell in the vanadium redox cell (Xiaoqiao Lu, 2001). With an increase in the \( H_2SO_4 \) concentration above 5M molar, a dramatic reduction in thermal precipitation could occur (M. Skyllas-Kazacos, \textit{et al.}, 1999).

### 2.2 The Vanadium Redox Flow Battery System Design

Figure 2.2 presents the workstation of the VRB system. The vanadium cell is placed on the top of the station, and two electrolyte storage tanks are in the second layer of the station. During cell operation, electrolytes are continuously circulated through the cell by a pumping loop at the second layer. The pump used in this work is a two-way peristaltic pump, which can pump positive and negative electrolytes with the same electrolyte flow rate of 50mL/min at the same time (MASTERFLEX\textsuperscript{®} 7520 series). Nitrogen gas continuously injects into both negative and positive storage tanks and empties into an ambient environment. Nitrogen pump/purge cycles are used to purge the amount of oxygen in the tanks to less than 0.1\% before operating the VRB system. Approximately nine cycles are needed for this as calculated by Eq. 2.3. \( P_a \) and \( P_h \) here are ambient temperatures and maximum temperatures of the tank, respectively.

\[
N_{\text{cycles}} = -\frac{4.0}{\log (P_a/P_h)}
\]
Figure 2.2: The workstation of the vanadium redox flow battery system.

The manufacturer of the flow battery cell used in this study is ElectroCell North America, Inc. The electrolyte inlet and outlet design of the cell is shown in Figure 2.3. The electrolytes pumped from negative and positive tanks flow into the cell from the bottom holes and flow out through the top holes of both cathode and anode half-cells. The effective area of the cell is defined by the effective area of 10cm$^2$ of graphite felt electrodes with 6mm thickness. In most cases, the 6mm thickness graphite felt received thermal pretreatment in a furnace at 400℃ for 30 hours. The porosity of graphite felt is approximately 92 % and it will reduce to around 61% after graphite felt is compressed to 33% of its original thickness (Hantao Zhou, 2006).
The membrane used in the cell is Nafion 117 (Dupont®). The membrane is then boiled in 80°C DI of water for 30 mins and then boiled in 80°C 1M of sulfuric acid solution for 30 mins for improving proton permeability. In the following, wipe the membrane with boiled DI water and store in DI water at the ambient environment before use.

Figure 2.3: The electrolyte flow design of the VRB cell.

Electrolytes flow through the graphite felt electrode inside a 2mm flow frame. Turbulent meshes with 0.5mm thickness are placed between the graphite felt electrode and membrane. The purpose of turbulent meshes is to create a turbulent flow in electrolytes, i.e. increase Reynolds number (Re) in the flow field for charge species in the electrolytes in the VRB cell. This may accelerate the reaction time and
enhance the performance of the cell. The side view of a positive half-cell of the VRB is shown as Fig 2.4. During the charge process, a positive electrolyte is circulated through the anode from the bottom hole into the flow frame, and the flow is out through the top hole back to the electrolyte storage tank.

Figure 2.4: Side view of the VRB cell.
2.3 Data Acquisition and Analysis

Generally, the cells were operated with five charge-discharge cycles to measure efficiencies, reaction times, and the amount of water transfer across the membrane of the VRBs. After one cycle of charge-discharge operation, the cell’s performance becomes steady. Figure 2.5 shows a plot of the charge-discharge cycle of the VRBs by applying a constant, current density of 60mA/cm², 50mL/min electrolyte flow rate, and 20mL electrolytes with original graphite felt and turbulent mesh inside the VRBs. Figure 2.6, the initial charge voltage and initial discharge voltages are 1.59V and 1.19V, respectively. The initial charge voltage and initial discharge voltage depend on internal losses of VRBs. The upper-limit voltage and lower-limit voltage of the cell are set to 1.86V and 0.8V, respectively. The fully charged and discharged voltages calculated by Eq. 1.4 and Eq. 1.6 set these two limits. Eq. 2.4 calculates average cell concentrations of all vanadium ions and protons.

\[ C_{\text{out},i}(t) = C_{\text{in},i}(t) + \frac{bN_{\text{cell}} i(t)}{F} \frac{1}{Q(t)} \quad [\text{mol/l}] \]

\[ C_{\text{cell},i}(t) = \frac{C_{\text{in},i}(t) + C_{\text{out},i}(t)}{2} \quad [\text{mol/l}] \quad 2.4 \]
Figure 2.5: The charge-discharge cycle of the VRB. Electrolyte flow rate is 50mL/min. Current density is 60mA/cm$^2$. Electrolyte volume is 20mL with original graphite felt and turbulent mesh.

The Arbin MITS Pro software continually recorded power, current capacity, current density, voltage, and voltage change for per second. The performance of flow battery could be measured by charge-discharge operation plot operated under constant current density. The definition of energy efficiencies, Coulombic efficiency, and voltage efficiency is as Eq. 2.5. Differently applied current densities, temperatures, and electrolyte flow rates all influence the efficiencies of the flow battery. The flow battery has higher efficiencies while applying lower current density for the cell and there is an optimal electrolyte flow rate of the flow battery. The concentration of
supporting sulfuric acid and proton ions influence density and viscosity of the vanadium electrolyte and subsequently impact the performance of VRBs (Y. Wen et al., 2006).

\[ \eta_e = \frac{\text{Discharge Energy (Wh)}}{\text{Charge Energy (Wh)}} \]

\[ \eta_c = \frac{\text{Discharge Capacity (Ah)}}{\text{Charge Capacity (Ah)}} \]

\[ \eta_v = \frac{\text{Energy Efficiency}}{\text{Current Efficiency}} \]

Differently applied constant current density and electrolyte flow rate changes the standard reaction times of VRBs, which can be calculated based on Eq. 2.6.

\[ t = \frac{CvVnF}{i} \]

The self-discharge rate is also an indicator of the performance of the flow battery. A longer self-discharge rate means improved performance from the battery, i.e. lower internal loss through crossover of VRBs. Self-discharge of the flow battery is the result of the crossover of active ions in electrolyte and water molecules through the Nafion membrane, so the OCV of the cell will gradually decrease without any electric connect. The vanadium ions and water transport continuously across the membrane depends on the SOC of the system (Chenxi Sun et al., 2010). Figure 2.6 is the plot of self-discharge for using original Nafion 117 and Nafion/SiO\textsubscript{2} hybrid membranes in the VRB. After OCV continuously decreased for a certain period of time, here 10 hours for Nafion 117 and 35 hours for Nafion/SiO\textsubscript{2}, OCV dropped quickly to approximately 0.7 V (Jingyu Xi et al., 2007). Self-discharge depends...
mainly on properties of the membrane, i.e. permeability of active ions through the membrane.

Figure 2.6: Open circuit voltage (OCV) of the VRB as a function of time at the state of charge (SOC) of 75%. From Jingyu Xi et al., 2007.

For analyzing the impact of using the turbulent mesh and the thermal graphite felt electrode in the VRB cell, we set four different tests. The operation conditions of four tests were shown as Table 2.1. In all tests, the electrolyte flow rate was 50mL/min, and the applied current density was 60mA/cm² during both charge and discharge processes.

Table 2.1: The operation conditions of Tests 1-4.

<table>
<thead>
<tr>
<th></th>
<th>Test #1</th>
<th>Test #2</th>
<th>Test #3</th>
<th>Test #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>With Turbulent Mesh</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Use Thermal Pretreatment</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Graphite Felt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.1 Repeatable Data of VRB System

The first objective of the work was to design and build a test station for measurement of performance on a flow battery, as described in Chapter 2. The first major experimental task was to develop the expertise needed in assembly of the test cell, and in preparation of the electrolyte and test station. This is critical to assure repeatable performance could be achieved and other experimental testing would yield reliable comparative results. Figure 3.1 shown here demonstrated repeatability was achieved. In this case, the effective planform area of the graphite felt electrode and polymer membrane were 10cm$^2$. The electrolyte flow rate was 50mL/min and the constant charge and discharge density was 60mA/cm$^2$ using original graphite felt with the turbulent mesh. The repeatable data of charge-discharge operation cycles of the VRB system using original graphite felt with turbulent mesh is shown in Figure 3.1. The Coulombic efficiency (CE), voltage efficiency (VE), energy efficiency (EE), initial charge voltage (ICV), and initial discharge voltage (IDCV) are shown in Table I. The upper limit voltage of the cell was set at 1.86V and the lower-limit voltage was set at 0.8V.

During the charge process, the voltage of the cell increased sharply to 1.86V while electrolytes were being fully charged. In the same way, the voltage of the cell decreased sharply to 0.8V while electrolytes were being fully discharged. The efficiencies of the cell became steady after the first cycle. The standard maximum error of efficiencies was 3.8\%, which is within an acceptable range. The operation time for the first cycle was slightly longer than the following cycles, and the efficiencies of the first cycles were the lowest compared with the others. The reason
for this was that it took time for the temperature increased to stabilize the region and for the vanadium electrolyte to become fully wetted into the porous structure of the graphite felt electrode.

Figure 3.1: Charge-discharge cycles of Test #1 VRBs. The applied current density was 60mA/cm². The electrolyte flow rate was 50mL/min, and the cell used original graphite felt with turbulent mesh.
Table 3.1: Efficiencies and initial voltages of Test #1.

<table>
<thead>
<tr>
<th></th>
<th>First Cycle</th>
<th>Second Cycle</th>
<th>Third Cycle</th>
<th>Forth Cycle</th>
<th>Fifth Cycle</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE</td>
<td>80.2%</td>
<td>87.3%</td>
<td>88.1%</td>
<td>89.0%</td>
<td>89.4%</td>
<td>86.8%</td>
</tr>
<tr>
<td>VE</td>
<td>63.9%</td>
<td>63.8%</td>
<td>62.5%</td>
<td>62.1%</td>
<td>63.1%</td>
<td>63.1%</td>
</tr>
<tr>
<td>EE</td>
<td>51.2%</td>
<td>55.7%</td>
<td>55.0%</td>
<td>55.2%</td>
<td>56.4%</td>
<td>54.7%</td>
</tr>
<tr>
<td>ICV</td>
<td>1.60V</td>
<td>1.57V</td>
<td>1.59V</td>
<td>1.60V</td>
<td>1.59V</td>
<td>1.59V</td>
</tr>
<tr>
<td>ICDV</td>
<td>1.23V</td>
<td>1.22V</td>
<td>1.19V</td>
<td>1.18V</td>
<td>.1.19V</td>
<td>1.20V</td>
</tr>
</tbody>
</table>

3.2 Turbulent Mesh Effect

Since the ionic charge losses in the electrolyte are a significant portion of the overall losses, one concept for minima of this loss is thorough the introduction of devices to enhance the liquid-phase transport of the electrolyte from the electrode to the membrane. For this purpose, a turbulent mesh (Note- flow is not truly turbulent, although the mesh is called a turbulence promoter by the manufacturer) was placed in the flow field between the graphite felt electrode and the membrane for enhancing convection of charge species in electrolytes. Figure 3.2 shows the charge-discharge voltage plots of Test #1 with turbulent mesh and Test #2 without turbulent mesh. The efficiencies, initial charge voltage ICV, and initial discharge voltages ICDV are shown in Table II. The operating conditions of the two experiments were identical when using the original graphite felt electrode, 50mL/min electrolyte flow rate, and 60mA/cm² applied current density. The rates of voltage change during the charge and discharge processes of Test#1 were just slightly faster than Test #2. Therefore, it the diffusion rates of charge species were not significantly improved by using the turbulent mesh inside the VRB cell, so the Coulombic efficiency in Test #1 had just been slightly improved. From Table II we know that the difference between initial
charge and initial discharge voltages was slightly lower in Test #2 without turbulent mesh. It means that the internal loss of the cell in Test #2 was lower than Test #1. In the Test#2, the bulk cell IR resistances were $0.286 \, \Omega \, \text{cm}^2$ and $0.298 \, \Omega \, \text{cm}^2$ during charge and discharge processes, respectively. The bulk cell IR resistances of Test#1 were $0.287 \, \Omega \, \text{cm}^2$ and $0.300 \, \Omega \, \text{cm}^2$ during charge and discharge processes, respectively. The reason might be that turbulent meshes slightly increased ohmic loss inside the cell, which would be the opposite of the desired effect. This may be because although the mesh enhances the flow orthogonal to the membrane, the proportion to and away from the membrane is equal, so the net effect may be close to zero. Alternative designs which asymmetrically alter the flow behavior are now being investigated. Additionally, the energy efficiencies of Test #1 and Test #2 were close. The upper-limit and lower-limit voltages of both tests were 1.86V and 0.8V, respectively.
Figure 3.2: The charge-discharge plots of Test #1 with turbulent mesh and Test #2 without turbulent mesh. The applied current density was 60mA/cm². The electrolyte flow rate was 50mL/min, and the cell used original graphite felt.
Table 3.2: Efficiencies and initial charge and discharge voltages of Test #1 and Test #2.

<table>
<thead>
<tr>
<th></th>
<th>Test #1 With Turbulent</th>
<th>Test #2 Without Turbulent</th>
</tr>
</thead>
<tbody>
<tr>
<td>QE</td>
<td>89.4%</td>
<td>88.0%</td>
</tr>
<tr>
<td>VE</td>
<td>63.1%</td>
<td>64.1%</td>
</tr>
<tr>
<td>EE</td>
<td>56.4%</td>
<td>56.4%</td>
</tr>
<tr>
<td>ICV</td>
<td>1.59V</td>
<td>1.55V</td>
</tr>
<tr>
<td>IDCV</td>
<td>1.19V</td>
<td>1.19V</td>
</tr>
</tbody>
</table>

The Arbin System also measured the self-discharge OCV of Test #2 without turbulent mesh. During the self-discharge process, vanadium species and water molecules continuously crossed over the membrane causing the change of OCV of the VRB cell. Figure 3.3 shows the OCV change of the VRB cell immediately after the cell attained a charged state of 90% SOC (1.86V). There are clearly two sharp decreasing steps in Figure 3.3. The first sharp decreasing step happened at about 60 hours and the second sharp decreasing step at about 78 hours. Chenxi Sun et al. pointed out the first sharp decreasing peak was associated with VO$_2^+$ ions disappearing in the positive electrolyte tank and the second sharp decreasing peak was associated with the V$^{2+}$ ions disappearing in the negative electrolyte tank during the self-discharge process (Chenxi Sun et al., 2010).
Figure 3.3 Self discharge open circuit voltage plot of Test #2 VRB cell.

The rates and directions of different vanadium species crossing over the membrane depend on the concentrations of different vanadium species in both positive and negative electrolyte storage tanks, i.e. depend on self-discharge times. Vanadium ions crossing through the membrane reacted with other vanadium species and influenced the concentrations of different vanadium species in both the positive and negative tanks (Chenxi Sun et al., 2010).
3.3 Thermal Pretreatment Graphite Felt Effect

The next major experimental goal was to investigate the impact of thermal pretreatment of the electrode. For this, the thermal pretreatment of the graphite felt electrode at 400°C for 30 hours was used. The other operation conditions were the same as Test #1. Figure 3.4 shows the plots of the charge-discharge cycles of Test #1 and Test #3. Efficiencies and initial charge voltage ICV and initial discharge voltage IDCV data are shown in Table III. The energy efficiency of Test #3 improved about 29% larger by using a thermal pretreatment graphite felt electrode. In the case of Test #3, the difference between the initial charge voltage and the initial discharge voltage was much lower compared with to Test #1. This means that the internal loss inside the cell in Test #3 had been reduced significantly by using the pretreatment graphite felt electrode. The reason might be that the thermal treatment increased more oxygen molecules combined on the surface of the graphite felt electrode, and this treatment significantly reduced activation loss of electrochemical reactions in the VRBs (B.E. Conway et al., 2002). Another reason might be that thermal pretreatment changed the crystal structure of the graphite felt electrode, which enhanced the wettability of the electrolyte inside graphite felt electrode, thus reducing the ionic resistance of the VRB cell (W.H. Wang et al., 2007). The cell with higher internal loss consumed more additional energy during the discharge process. Therefore, the energy efficiency of Test #1 was much lower than Test #3. Charge transfer rates were similar in these two cases by observing Figure 3.4 and Coulombic efficiencies were also similar. The upper-limit voltage of Test #3 was set at 1.7V. The lower-limit voltage of Test #3 was also set at 0.8V.
Figure 3.4: Charge-discharge plots of Test #1 original graphite felt and Test #3 pretreatment graphite felt at 400°C for 30 hours. The applied current density was 60 mA/cm². The electrolyte flow rate was 50 mL/min, and the cell used turbulent mesh.

Table 3.3: Efficiencies and initial charge and discharge voltage of Test #1 and Test #3.

<table>
<thead>
<tr>
<th></th>
<th>Test #1 Original Graphite Felt</th>
<th>Test #3 Thermal Pretreatment graphite felt</th>
</tr>
</thead>
<tbody>
<tr>
<td>QE</td>
<td>89.4%</td>
<td>88.9%</td>
</tr>
<tr>
<td>VE</td>
<td>63.1%</td>
<td>82.2%</td>
</tr>
<tr>
<td>EE</td>
<td>56.4%</td>
<td>73.1%</td>
</tr>
<tr>
<td>ICV</td>
<td>1.59V</td>
<td>1.35V</td>
</tr>
<tr>
<td>IDCV</td>
<td>1.19V</td>
<td>1.42V</td>
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</tbody>
</table>
Figure 3.5 compares charge-discharge plots between Test #3 and Test #4, which also used pretreatment heating graphite felt at 400°C for 30 hours, but Test #4 was without using turbulent mesh inside the VRB cell. The energy efficiency of Test #4 was higher than Test #3, whereas Coulombic efficiencies between the two cases were close. The reason might be that the internal IR loss of Test #3 using additional turbulent mesh was higher than Test #4. The lower voltage difference between initial charge and initial discharge also confirmed the higher internal loss in Test #3. Then the higher energy consumption by the internal loss in Test #3 caused the lower energy efficiency. The upper-limit voltage and lower-limit voltages of Test #3 and Test #4 were all set to 1.7V and 0.8V, respectively.
Figure 3.5: The charge-discharge plots of Test #3 and Test #4. The applied current density was 60 mA/cm². The electrolyte flow rate was 50 mL/min, and the cells all used thermal pretreatment graphite felt at 400°C for 30 hours.

Table 3.4: Efficiencies and initial charge and discharge voltages of Test #3 and Test #4.

<table>
<thead>
<tr>
<th></th>
<th>Test #3 Thermal Pretreatment Graphite Felt With Mesh</th>
<th>Test #4 Thermal Pretreatment Graphite Felt Without Mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>QE</td>
<td>88.9%</td>
<td>88.2%</td>
</tr>
<tr>
<td>VE</td>
<td>82.2%</td>
<td>87.6%</td>
</tr>
<tr>
<td>EE</td>
<td>73.1%</td>
<td>77.3%</td>
</tr>
<tr>
<td>ICV</td>
<td>1.35V</td>
<td>1.28V</td>
</tr>
<tr>
<td>IDCV</td>
<td>1.42V</td>
<td>1.47V</td>
</tr>
</tbody>
</table>
Figure 3.6 – 3.8 shows the continuously charge-discharge cycles of Test #2, Test #3, and Test #4.

Figure 3.6: Charge-discharge cycles of Test #2. The applied current density was 60mA/cm$^2$; the electrolyte flow rate was 50mL/min, and the cell used turbulent meshes.
Figure 3.7: Charge-discharge cycles of Test #3. The applied current density was 60mA/cm$^2$; the electrolyte flow rate was 50mL/min, and the cell used thermal pretreatment graphite felt at 400°C for 30 hours with turbulent meshes.
Figure 3.8: Charge-discharge cycles of Test #4. The applied current density was 60mA/cm$^2$; the electrolyte flow rate was 50mL/min, and the cell used thermal pretreatment graphite felt at 400°C for 30 hours without turbulent meshes.

Approximately 15% of the volume of the electrolyte transferred from negative to positive tanks after 14 hours and five cycles of charge-discharge. The water transport mechanism in VRBs is complicated, a function of the concentration of different vanadium species, i.e. SOC. Generally, the net amount of vanadium and water is transferred from negative to positive electrolyte tank during long-term cycles of charge-discharge operation (Chenxi Sun et al., 2010).
4.1 Conclusions

The vanadium redox flow battery system designed, constructed, and tested in our lab was able to achieve repeatable and competitive results. Then the impact of the thermal pretreatment step for the graphite felt electrode and the usage of turbulent mesh for diffusion rates of charge species in the electrolyte were identified. The thermal pretreatment was the crucial step to enhance the energy efficiency of a VRB cell. The energy efficiency of the VRB could attain 77% by using the thermal pretreatment graphite felt electrode, which was 29.5% larger than the VRB using non-treatment graphite felt electrode for the same test conditions. The energy consumption by internal losses was significantly reduced by the usage of thermal pretreatment graphite felt. Coulombic efficiencies were similar in both cases. The usage of turbulent promoter only slightly increased Coulombic efficiency, indicating the anticipated improvement in convection of the charged species toward the membrane was limited. Also, the bulk cell IR resistance slightly increased by using the turbulent promoter, and the energy efficiency slightly decreased. The energy efficiency of the cell was 5% lower using turbulent mesh with the thermal pretreatment graphite felt electrode of the same test conditions.

The amount of water transport and OCV of the self-discharge process were also recorded. After 14 hours charge-discharge operation, 15% of the water volume was transferred across the 10cm$^2$ active surface Nafion membrane from negative to positive storage tanks. During the self-discharge process, the open circuit voltage OCV gradually decreased to 1.2V from 1.5V for 60 hours after the cell had been
charged to 90% SOC. After 90 hours, the OCV of the cell decreased to approximately 0.2V.

### 4.2 Future Work

The VRB system we built has proven to be a repeatable and reliable system. Since the usage of present turbulent mesh did not significantly improve the performance, there is room to design better concepts of turbulent promoters inside the cell to accelerate the diffusion rates of charge species from the reaction surface in the electrode to the membrane. Also, a diverse measurement is needed for the VRB cell to accurately measure and model for vanadium species and water molecules crossovers through the membrane.

**Side Reaction Measurement of $O^2$ and $H^2$**

Side reactions of $O^2$ and $H^2$ gas bubbles from water molecules cause current loss inside VRBs on anode and cathode during the charge process, respectively. Literature had simulated the influence of $O^2$ and $H^2$ gas bubbles on the graphite felt electrode. However, it is necessary to visualize the actually gas bubble distribution image inside the VRB cell. Experimental images and analyses of gas distribution and the simulation work could verify the actual impact of $O^2$ and $H^2$ gas reactions inside VRBs. The neutron image system may help to identify the interface of gas bubbles, electrolytes, and electrodes inside both positive and negative half-cells. It may help to model accurately the operation systems of all kinds flow batteries. Also, the influence and reactions of gas bubbles in electrolytes is not clear. Gas bubbles inside the cell may not only block the electrochemical reaction between electrodes and electrolytes, but they may also consume current and thereby cause reduction reactions. The
influence of side reactions needs to be discussed more carefully inside flow batteries to establish more accurate modeling work.

**Turbulent Promoter**

A turbulent promoter could increase turbulent flow and improve the mass transport of charge species in the electrolytes. However, there is no optimal design of turbulent mesh, which could significantly improve the performance of VRBs. The turbulent promoter needs to increase turbulent flow but without increasing internal resistance of the cell. It may be possible to utilize current conductive material as the turbulent promoter to increase Reynold’s number and the electrochemical reaction area at the same time. The CFD modeling may help to build up more efficient turbulent promoter to reduce mass transport loss for the cell.

**Water Mechanism in VRB Cell**

Water molecules crossover the membrane by vanadium and proton ions’ dragging force and osmosis force change the concentrations of electrolytes. An additional step will be needed to withdraw back the water molecules from positive half-cells to negative half-cells in the long-term system operation. Besides, the water crossover also worsens the self-discharge problem of the flow battery. Modifying the membrane could reduce the water transport, but generally increase internal resistance. Since osmosis forces dominate water molecules’ crossover problem, it may beneficial to utilize pressure difference or gravity difference between two half-cells to reverse water transport through the membrane. Actually, the water mechanism inside the cell depends on concentration changes of electrolyte and properties of the membrane. It is not difficult to measure and calculate the concentration change of vanadium ions and water molecules transfer, but how to verify the water transfer mechanism and
calculate water molecules transfer by osmosis force is not so clear. What is needed is the ability to measure permeability of proton and water molecules through the membrane and establish a model to simulate water transfer by all forces.

2-D Model of VRB Cell

In literature, there is a 1-D model to define concentration differences of vanadium species in both positive and negative half-cells. In flow battery systems, more work is needed to establish 2-D work, which may include water transport mechanisms and triple-phase area in graphite felt electrodes to simulate efficiencies and voltages of VRBs under different operation conditions and comportment properties. 2-D modeling work is also beneficial to define concentration distribution and calculate concentration loss inside the cell and verify water transport mechanisms inside VRBs.
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