Performance of Nafion® N115, Nafion® NR-212, and Nafion® NR-211 in a 1 kW Class All Vanadium Mixed Acid Redox Flow Battery

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ABSTRACT

Three Nafion® membranes of similar composition but different thicknesses were operated in a 3-cell 1kW class all vanadium mixed acid redox flow battery. The influence of current density on the charge/discharge characteristics, coulombic and energy efficiency, capacity fade, operating temperature and pressure drop in the flow circuit will be discussed and correlated to the Nafion® membrane thickness. Material costs associated with the Nafion® membranes, ease of handling the membranes, and performance impacts will also be discussed.

Key words: Vanadium redox flow battery, Nafion® membranes, electrical performance, cost

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1. Introduction

The increasing need to integrate renewable energy with the current electricity grid has made energy storage systems play a more prominent role in bridging the gap between state of the art technologies and a clean sustainable future in grid utilization and reliability [1]. Among the most promising energy storage technologies are redox flow batteries (RFBs) [2-3]. Redox flow batteries are capable of storing a large quantity of electricity (multi-MWs/MWhs) in a simple design [1,4]. A redox flow battery is a reversible energy storage system which converts chemical energy into electrical energy while the electrolyte, which consists of dissolved electroactive species in solution, is circulated through the electrochemical cell. Between the electrodes is an ionic conducting membrane or separator that allows the transport of selective species in the cell. Unlike conventional batteries, a redox flow battery power and energy specifications can be scaled independently with the energy being proportional to the amount of redox active species in the electrolyte (storage tank volume and electrolyte concentration) and the power proportional to the reactor size. In addition, the storage of reactive materials in separate tanks allows the flowing electrolyte to carry away unwanted heat generated during operation; this leads to improved safety and ease of thermal management designs in large scale systems.

The first redox flow battery was developed by NASA over 35 years ago based on the $\text{Fe}^{2+/3+}$ - $\text{Cr}^{2+/3+}$ system [5]. A $\text{Fe}^{2+/3+}$ halide solution electrolyte was used in the positive half-cell and a $\text{Cr}^{2+/3+}$ halide solution was used in the negative. Severe cross contamination issues were encountered which lead to the development of two important redox flow battery system, namely GEN 2 Fe/Cr and the all vanadium flow battery (VRB) [6-7]. The GEN 2 Fe/Cr system utilized

a mixed electrolyte as both the positive and negative electrolyte whereas the VRB enlists the same element, i.e. V, in both the positive and negative electrolyte.

Significant progress has been made on advancing the redox flow batteries with the demonstration of multi-MWh systems [8] but the current technologies do not meet all the performance and cost requirements needed for a broad market penetration. The VRB system has made significant improvements over the years including excellent electrochemical reversibility, high round-trip efficiency, and negligible cross-contamination between positive and negative electrodes [8], but the technology is still limited by vanadium ion stability and solubility over a broad temperature range. This limits the system to a lower energy density and a narrow operating temperature window. Active heat management systems are needed which increase parasitic energy losses and lowers the overall system efficiency. The high corrosive nature of V^{5+} in solution and the need for relatively high cost Nafion® membranes are other issues that have hindered the VRB system to present.

Recent developments on a mixed acid VRB system have shown significant improvement in active materials concentration and operation temperature range over sulfate acid based VRBs [9-12]. One major issue shared amongst all VRBs systems, however, is the use of the high cost Nafion® membranes. Lower cost Nafion® membranes could open the VRB technology to a broader market by lowering cost and/or improving system performance. Thinner, lower cost Nafion® membranes utilizing the mixed acid system were investigated on a 1 kW class stack. This paper reports the detail of this work.

2. Experimental

The starting sources for the mixed acid electrolyte (2M V + 2M S + 5M Cl) were VOSO₄·xH₂O (Noah Technologies, San Antonio, TX, 99.5%, x = 2.0~2.3), HCl (Sigma-Aldrich, 37%), and H₂SO₄ (Sigma-Aldrich, 95.8%).

A 1 kW class prototype stack was fabricated using 3 repeated unit cells, aluminum end plates, tin coated copper current collector plates, and bolts [11]. The integrated design combines the anode and cathode flow frames, two porous graphite felt sheets (SGL, GFD4.6), and a thin solid graphite plate (SGL expanded graphite, TF6) into a single component. The graphite felt sheets were thermally heat treated in air at 400°C for 6 hours and then compressed by ~ 15% during assembly. Nafion® membranes (N115, NR-212, and NR-211) were soaked in deionized water for 14 hours prior to assembly. Active area of cells was 780 cm² and overall stack dimensions are 31(w) x 44 (h) x 40 (l) cm.

Stack performance was measured using an in house designed test system, Figure 1 [11]. The test system includes a 3 cell stack, two electrolyte reservoir tanks, two centrifugal pumps (Finnish Thompson, DB4V-T-M613), two flow meters (Omega FMG83 Magmeters), pressure (Measurement Specialties MSP-300-100-P-1-N-1) and temperature sensors, a transfer pump, and valves. Anolyte and catholyte volumes were 6 L and contained in high density polyethylene tanks with a capacity of 19 L. Each tank is equipped with supply and return ports, and an additional four ports for pressure and temperature sensors, a transfer line, and a nitrogen purge line. Teflon coated type N thermocouples (1/8") were inserted inside each tank to measure the electrolyte temperature. The two electrolyte tanks are connected pneumatically by a 1/4" tube to avoid mechanical pressure variation attributed to the electrolyte volume change as a result of ionic or water transport across the Nafion® membrane during operation. Pressure drop in the

cathode and anode was measured using a pressure transducer placed between the pump and the stack inlet, respectively.

Electrochemical performance was evaluated using an Arbin Instruments, BT-2000, battery tester. Cell voltages, flow and temperature measurements, and pressure were monitored using the Arbin battery tester. The system was purged with nitrogen and sealed before evaluation to prevent oxidation of active species with air. The redox flow battery was cycled between 1.65 and 1.2 V at a current density of 80 mA/cm², between 1.75 and 1.1 V at 160 mA/cm², and between 1.80 and 1.05 V at 240 mA/cm². The voltage range differs to compensate for the different ohmic losses and ensure that the state of charge (SOC) range is held constant between 15 and 85%. Anolyte and catholyte were totally remixed and charged prior to each test to ensure identical initial test conditions in order to make accurate comparisons. Prior to remixing, the electrolytes were deep discharged to 0.8 V/cell at 80 mA/cm² to minimize the generation of heat.

Efficiencies are defined as:

$$\text{Stack coulombic efficiency (CE)} = \frac{\int i_d dt}{\int i_c dt} \quad (1)$$

$$\text{Stack energy efficiency (EE)} = \frac{\int p_d dt}{\int p_c dt} = \frac{\int V_d i_d dt}{\int V_c i_c dt} \quad (2)$$

where i denotes current, p is power, V is voltage, and c , and d denote charging and discharging, respectively.

Nafion® membranes used in this study were N115, NR-212, and NR-211 which are commercially available at Ion Power [13]. The three different membranes are similar compositionally but differ in thickness. Nafion® N115 is extruded whereas NR-212 and NR-211 are cast. The last number in the product code signifies the thickness in mils, N115 is 5 mils,

NR-212 is 2 mils, and NR-211 is 1 mil thick. As stated earlier, these membranes were used in identical 3-cell stacks and the results are reported below. Current densities of 80, 160, and 240 mA/cm² were evaluated on 3-cell stacks fabricated with Nafion® N115, NR-212, and NR-211, Nafion N115 was omitted from evaluation at 240 mA/cm² due to limited performance. Table 1 lists the specifications of the 1 kW class stack.

3. Results and Discussion

Operation current density and electrolyte flow rate are two important parameters that influence the performance of the flow battery stack. Operating at higher current densities dictates overall power of the system but tends to limit performance due to increased Ohmic and polarization losses. Nafion® membranes evaluated at various current densities are the focus of this study and will be reported in greater detail in the following sections. Electrolyte flow rate also influences performance as well as pumping power consumption. Higher flow rates decrease mass transport losses [14] especially at high current densities, thereby improving stack performance. Therefore, optimal balance between current density operation and flow rate is necessary to maximize overall system efficiency. A constant flow rate was used in this study (1.2 L/min) with minimal pressure drop (< 10 psi) to evaluate the influence of current density on stack performance. The influence of current density, method to increase the flow rate with minimal pressure drop, and the resultant system performance will be addressed in more detail in subsequent papers.

The charge/discharge voltage and power cycling performance at 160 mA/cm² and a flow rate of 1.2 L/min for the three Nafion® membranes is shown in Figure 2. The difference in voltage between the three membranes is nearly identical over the measured range indicating the

voltage drop is dominated by Ohmic losses. The largest voltage difference occurred between Nafion® N115 and Nafion® NR-212 and is attributed to the reduction in the membrane thickness from approximately 5 mils ($\sim 125\ \mu\text{m}$) to 2 mils ($\sim 50\ \mu\text{m}$). A much smaller voltage difference occurred between the Nafion® NR-212 and Nafion® NR-211 and is most likely that the ohmic losses attributed from the membrane are no longer the dominate loss at $160\ \text{mA}/\text{cm}^2$. At a constant current discharge of $160\ \text{mA}/\text{cm}^2$, the minimum power delivered to the stacks with different Nafion® membranes was 400 W at an end voltage of 3.3 V, Figure 2b.

Figure 3 shows the charge/discharge voltage and power cycling performance of the Nafion® NR-212 membrane at 80, 160, and $240\ \text{mA}/\text{cm}^2$ and a flow rate of 1.2 L/min. The voltage difference between the three current conditions is again similar over the majority of the measured range inferring that the voltage drop is dominated by ohmic losses. The minimum power the stack delivered at 80, 160, and $240\ \text{mA}/\text{cm}^2$ was 200, 400, and nearly 600 W, respectively. As the current density was increased by three-fold, the minimum power nearly tripled. The increased power at higher current densities, however, attributes to a lower energy efficiency which will be discussed in more detail in the following sections.

Plotted in Figure 4 is the discharge energy (Wh) for the three Nafion® membranes as a function of current density (80, 160, and $240\ \text{mA}/\text{cm}^2$). In all cases, the discharge energy was decreased with increasing current density. The Nafion® N115 showed the largest drop, $\sim 32\%$, by increasing the current density from $80\ \text{mA}/\text{cm}^2$ to $160\ \text{mA}/\text{cm}^2$. Membranes of Nafion® NR-212 and NR-211, however, showed a less dramatic decrease, $\sim 7\%$, at the same conditions. A more prominent drop in the discharge energy, $\sim 15\text{-}18\%$, for both the Nafion® NR-212 and NR-211 occurred between $160\ \text{mA}/\text{cm}^2$ and $240\ \text{mA}/\text{cm}^2$.

The discharge capacity (Ah/L) for the three Nafion® membranes as a function of current density is also shown in Figure 5. The discharge capacity (Ah/L) increases with decreasing Nafion® membrane thickness. The thinnest membranes also show more capacity for the same given current density.

Shown in Figure 6 is the 3-cell stack energy efficiency of the three Nafion® membranes as a function of current density. In general, the Nafion® NR-212 and 211 show very similar behavior over the entire current density regime studied. The Nafion N-115 showed a substantial decrease in energy efficiency in comparison to the Nafion® NR-212 and 211. This again suggests that the ohmic loss contribution from the membrane is significant for the thick N115 membrane but is less significant for the thinner membranes, NR-212 and NR-211. This also suggests that other loss mechanisms are more predominate for the thinner membranes, i.e. ohmic losses associated with the electrolyte, polarization losses at the electrode, etc. As discussed earlier, a means to improve the mass transfer kinetics at high current densities is to increase the flow rate which will be studied in the near future and published in future reports.

Figure 7 shows the ambient cyclic performance of the 3-cell systems utilizing the three Nafion® membranes at 160 mA/cm^2 . No external thermal management was used in these studies but the overall temperature was predominately dictated by the operating current density which will be discussed in further detail in the following sections. The coulombic and energy efficiencies remain constant over 20 cycles indicating that the system is capable of operating reliably over a significant time period. The coulombic efficiencies were typical for this system with a range of ~ 97-98%. The energy efficiency was significantly larger for the Nafion NR-212 and NR-211, ~ 82%, than the Nafion N115, ~75%. This again signifies the loss associated with using the thicker membrane.

The maximum discharge capacity or capacity fade through cycling for the three Nafion® membranes at 160 mA/cm² is shown in Figure 8. The three Nafion® membranes all behave in a similar manner as typically observed in this system at the given conditions. The three membranes show approximately 22% reduction in capacity in the first 25 cycles and approximately 35% reduction in the first 50 cycles.

The electrolyte temperature was measured by inserting a sealed thermocouple into the positive and negative tanks during operation. The highest temperature that the electrolyte was operated during cyclic performance was recorded and is plotted in Figure 9 for the three Nafion® membranes operated at 80 mA/cm², 160 mA/cm², and 240 mA/cm². The electrolyte temperature was predominately dependent on the current density and independent of the type of membrane. As the current density was increased at 80 mA/cm² intervals the temperature was increased in steps of approximately 5°C. At 80 mA/cm², 160 mA/cm², and 240 mA/cm², the electrolyte temperature was approximately 35°C, 40°C, and 45°C, respectively.

Pressure transducers were placed between the pump and the stack inlet on both the anode and cathode side to measure the pressure drop during operating at various conditions, the results for the three Nafion® membranes at the three different current densities is shown in Figure 10. The pressure drops also appear to be independent of the type of membrane but mostly dependent on the current density. The highest current densities tend to run warmer as discussed above which reduces the viscosity of the electrolyte thereby reducing the pressure drop in the circuit. The pressure drop at 80 mA/cm², 160 mA/cm², and 240 mA/cm² was approximately 8 psi, 7.2 psi, and 6.5 psi, respectively. As shown in Figure 10, the increased current density minimizes the pressure drop which allows one to further increase the flow rate for a specifically designed system. In this study, the pressure drop was limited to 10 psi to minimize pump losses. The

pressure drop was approximately doubled with a 2 fold increase in flow rate. Therefore, desired flow rates of 3-5 fold that were studied here could not be accomplished by simply increasing the current density. Rather, specifically designed flow patterns to dramatically reduce the pressure drop need to be explored and will be reported in future publications.

The cost of the Nafion® membrane can be on the order of 25-50% of the total material cost in a redox flow battery depending on the design and/or application. It is therefore important to minimize the cost to enhance system performance (\$/kWh) and open the redox flow battery to a broader market. The cost of the three Nafion® membranes was calculated [13] based on sheets of 0.3 meters wide by 20 meters long, the cost analysis is shown in Figure 11. The cost of the Nafion® NR-212 is approximately 50% lower than the Nafion® N115 and about 15% greater than the Nafion® NR-211. Utilizing the Nafion® NR-212 over the more typically used Nafion® N115 would result in a 12-25% reduction in material cost. Handling and fabricating stacks with Nafion® NR-212 was found to be very similar to the Nafion® N115. Therefore, the Nafion® NR-212 could be used as a direct replacement for Nafion® N115 with the added benefits of improved performance and lower costs. The thinner Nafion® NR-211 was the lowest cost membrane studied but was also found to be most difficult to handle. The thin membrane tended to adhere to itself and make stack fabrication more cumbersome. Nafion® NR-212 would most likely be the membrane of choice for the conditions studied here (i.e. $< 240 \text{ mA/cm}^2$) due to the improved performance, lower cost, and ease of fabrication. However, Nafion® NR-211 could become more importance in use as higher current densities are explored and the ohmic losses from the membrane become more predominate and with improved fabrication methods.

Conclusions

The use of thinner Nafion® membranes (NR-212 and NR-211) was found to have better electrical performance and significantly lower cost in comparison to the thicker Nafion® N115 membrane. Other important operating parameters such as electrolyte temperature and pressure drop in the flow field were comparable for the three Nafion® membranes. Electrical performance of Nafion® NR-212 and NR-211 were comparable over the current densities studied but the Nafion® NR-212 was found to be easier to handle and fabricate into stack components and would be the optimum membrane of choice for conditions studied. However, utilizing the thinnest Nafion® NR-212 membrane may become advantageous at higher current densities and as advanced manufacturing methods become available that assists in handling and fabricating stacks.

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Figure Captions:

- Figure 1. 1 kW vanadium redox flow battery testing system
- Figure 2. Charge and discharge performance of the 3-cell stacks fabricated with three Nafion® membranes at 160 mA/cm² and a flow rate of 1.2 L/min a) charge and discharge curves and b) discharge power curves.
- Figure 3. Charge and discharge performance of the 3-cell stack fabricated with Nafion® NR-212 at 80, 160, and 240 mA/cm² and a flow rate of 1.2 L/min a) charge and discharge curves and b) discharge power curves.
- Figure 4. Discharge energy of 3-cell stacks for the three Nafion® membranes at 80, 160, and 240 mA/cm² and a flow rate of 1.2 L/min.
- Figure 5. Discharge capacity of 3-cell stacks for the three Nafion® membranes at 80, 160, and 240 mA/cm² and a flow rate of 1.2 L/min.
- Figure 6. Stack energy efficiency of 3-cell stacks for the three Nafion® membranes at 80, 160, and 240 mA/cm² and a flow rate of 1.2 L/min.
- Figure 7. Coulombic and energy efficiency as a function of 20 charge/discharge cycles for 3-cell stacks utilizing three Nafion® membranes at 160 mA/cm² and a flow rate of 1.2 L/min.
- Figure 8. Maximum discharge capacity as a function of charge/discharge cycles for 3-cell stacks utilizing three Nafion® membranes at 160 mA/cm² and a flow rate of 1.2 L/min.
- Figure 9. Electrolyte temperature during operation of 3-cell stacks for the three Nafion® membranes at 80, 160, and 240 mA/cm² and a flow rate of 1.2 L/min.
- Figure 10. Maximum pressure drop of 3-cell stacks for the three Nafion® membranes at 80, 160, and 240 mA/cm² and a flow rate of 1.2 L/min.
- Figure 11. Unit cost of the three Nafion® membranes with dimensions of 0.3 meters wide by 20 meters long.

Table 1: Specification of 1 kW class stack

Dimensions (cm)	31 (W) x 44 (H) x 40 (L)
Active area (cm ²)	780
Number of cells	3
Electrode	Graphite felt (SGL GFD4.6) SIGRACET® expanded graphite (TF6)
Flow frame	PVC (polyvinyl chloride)
Membrane	Nafion® N115, NR-212, and NR-211
End plate	Aluminum
Power at 160mA/cm ²	~ 0.5 kW