Safety Characterization of Flow Battery of Two Chemistries

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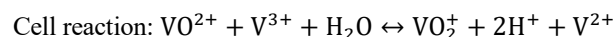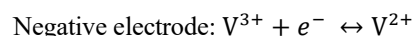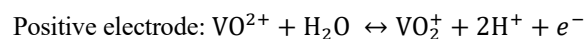judy.jeevarajan@ul.org

Abstract

Flow batteries are becoming more common in grid energy storage systems around the world. There are several flow battery chemistries that are being studied and some of the chemistries have been commercialized. Flow batteries consist of liquid electrolytes contained in two tanks or reservoirs. They are aqueous systems and the voltage associated with any single flow battery for the various chemistries used today is less than or equal to 2 V. The quantity of electrolyte used determines the capacity. For stationary grid energy storage applications, where weight and volume are not significant concerns, they are a good candidate, due to their much lower costs compared to other rechargeable battery systems. The performance of flow batteries has been of interest to researchers and the refinement of this property has been in work for quite some time. However, the safety of these systems is not studied widely. Safety standards typically tend to study the flammability of the electrolytes rather than studying the cell or system as a whole. The Electrochemical Safety Research Institute (ESRI) at UL Research Institutes has carried out performance and safety characterization tests on two flow battery chemistries. They are the vanadium system and the zinc-bromine system**.

Introduction

Redox flow batteries (RFBs) are currently used in large megawatt- and gigawatt-size grid energy storage systems. They store energy in electrolyte solutions which contain two redox couples that are pumped through the battery cell stack. Different redox couples can be utilized, such as V/V, Zn/Br$_2$, V/Br$_2$, S/Br$_2$, and Fe/Cr which influence the performance metrics of the batteries.[1] The energy stored by RFBs depends on the volume of the electrolytes in the tanks and the power depends on the size of the electrochemical cell stack. The specific energy of RFBs is relatively low compared to e.g., lithium-ion batteries, which generally limits RFBs' applications to stationary systems. The advantages of flow batteries include low cost, high cycle life, design flexibility and tolerance to deep discharges.[2] The factors and components affecting flow battery performance have been extensively studied but not the safety under off-nominal conditions. It is usually assumed that the high heat capacity of the aqueous electrolyte can prevent temperature rise. Moreover, the toxicity of the gases released, or the degradation of the flow battery components has not been widely investigated.

The vanadium redox flow battery (VRFB) is the most widely researched of the different flow battery chemistries and is already in a mature state for grid-level applications.[2, 3] The first VRFB was originally developed by Skyllas-Kazacos and coworkers at the University of New South Wales in Australia. The VRFB consists of two electrolyte reservoirs and a cell stack in which the two electrodes and respective electrolytes are separated from each other by an ion-exchange membrane (Figure 1). A solution of vanadium in a sulfuric acid supporting electrolyte is used in both half-cells, which has the advantage of eliminating the risk of electrolyte cross-contamination.[1] The negative half-cell utilizes the V^{2+}/V^{3+} redox couple and the positive half-cell the VO^{2+}/VO$_2^+$ couple, yielding a standard cell voltage of 1.26 V at 25 °C through the following reactions:[1]

Positive electrode: $VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^-$

Negative electrode: $V^{3+} + e^- \leftrightarrow V^{2+}$

Cell reaction: $VO^{2+} + V^{3+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + V^{2+}$

A feature of the VRFB electrolytes is the distinct colors of each of the different vanadium oxidation states, with V(II) being violet, V(III) green, V(IV) blue, and V(V) yellow.[4] This allows visual qualitative state of charge (SOC) determination and enables quantitative determination using spectroscopic measurements.[4]
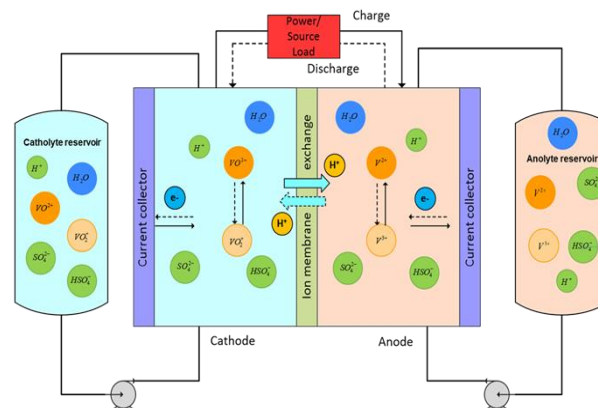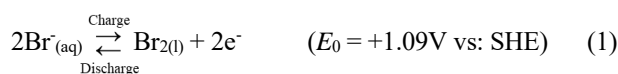

Figure 1. Schematic of a vanadium redox flow battery

Graphitic and carbonaceous materials are used as the electrodes for both the positive and negative half-cells due to their ability to withstand the highly corrosive electrolyte. The energy density of the VRFB system is limited by the solubility of the various vanadium species in the acidic
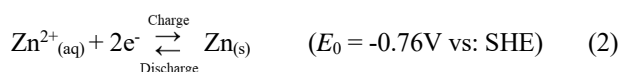
electrolyte within the battery operating temperature range.[1] Therefore, some of the recent VRFB systems utilize a mixed sulfuric acid-hydrochloric acid supporting electrolyte to increase the solubility of the vanadium species, thereby increasing the energy density and reducing issues with precipitation.[1, 5] However, the addition of hydrochloric acid into the electrolyte is associated with a risk of chlorine gas evolution, especially in case the battery is exposed to off-nominal conditions.[6]

Unlike the vanadium RFB system that has four different oxidation states, the zinc-bromine (Zn/Br_2) flow battery involves one solid phase and one liquid phase of active species.[7] The fundamental electrochemical reactions of the Zn/Br_2 RFB can be described as follows:
At the positive electrode:

$$2Br^-_{(aq)} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Br_{2(l)} + 2e^- \qquad (E_0 = +1.09V \text{ vs: SHE}) \qquad (1)$$

At the negative electrode:

$$Zn^{2+}_{(aq)} + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Zn_{(s)} \qquad (E_0 = -0.76V \text{ vs: SHE}) \qquad (2)$$

The overall cell reaction:

$$ZnBr_{2(aq)} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Zn_{(s)} + Br_{2(l)} \qquad (E_{cell} = +1.85V \text{ vs: SHE}) \qquad (3)$$
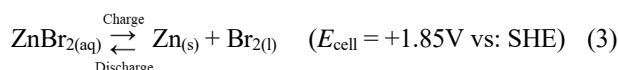
Figure 2 is a schematic of the Zn/Br_2 RFB. During charging, the bromide ions are oxidized to liquid bromine, Br_2 at the positive electrode and the Zn^{2+} is reduced to metallic zinc, Zn^0, at the negative electrode. The opposite reactions occur during the discharging process. The redox reactions occur in the interface of electrolyte and electrode, in which the metallic Zn is electrodeposited on the electrode surface during charging and is dissolved back in the electrolyte during the discharge process.[2]
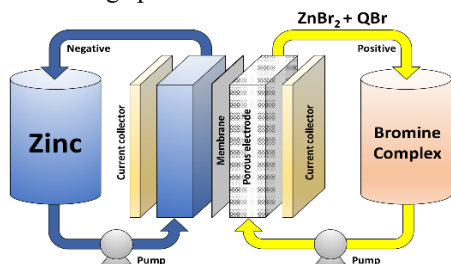

Figure 2. Schematic of the Zn/Br_2 RFB.

The bromine formed is sequestered and prevented from going into the vapor phase with the help of a complexing agent such as *N*-methyl-*N*-ethyl pyrrolidinium bromide (MEP) or *N*-methyl *N*-ethyl morpholinium bromide (MEM).[4–6] Furthermore, due to the higher density of these complex polybromide species, permeation of bromine and bromine aggregation across the ion exchange membrane is impeded.[4] An elevated conductivity in this system is crucial to avoid ohmic losses.[2] In addition, the operating pH range of most Zn/Br_2 commercial systems is between 1–3.5.[6] The

narrow pH range is carefully controlled throughout the operation, to avoid the formation of bromate (pH >3), solid zinc oxide (pH >6), as well as prevent hydrogen evolution (pH <1) which can lower the coulombic efficiencies which in turn lower the cyclability of the system.[1, 3]

Experimental

The lab scale vanadium flow battery was built using typical components used for a fuel cell. A photo of the lab scale system is shown in Figure 3.
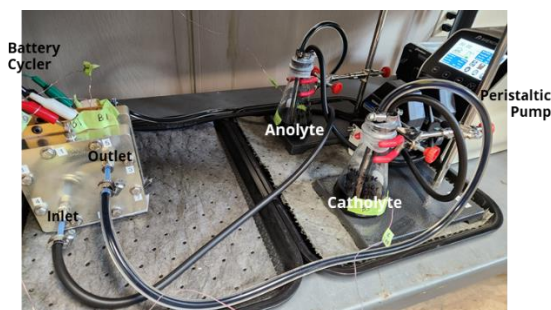

Figure 3. Lab-scale vanadium redox flow battery.

Vanadium sulfate solution (1M $VOSO_4$ and 3M H_2SO_4) was used as the catholyte and anolyte. Since the electrolyte has a charge of 3.5, pre-charge of the catholyte needs to be performed in order to have the relevant oxidation state of V^{5+} for the redox reaction. The catholyte flask had twice the volume of the anolyte during this pre-charge stage. After the cell was charged to 1.7V, half of the volume of the catholyte was removed. The cell consisted of typical acid fuel cell hardware with a triple serpentine flow pattern and an active area of 50 cm^2. The electrode was Sigracell carbon felt with a thickness of 2.5 mm and 90% porosity and a surface area of 0.4 m^2/g. The membrane was Nafion 212 with a thickness of 0.8 micron and a conductivity of 0.1 S/cm. A neoprene rubber gasket of 1/16" thickness was used. The flow rate of the electrolytes was 50 ml/min. The resulting flow battery cell had a voltage of about 1.26 V and a capacity of 2.0 Ah. The cells were cycled between 1.7 V and 0.7 V using a charge and discharge current of ~1 A (20 mA/cm^2).

The off-nominal safety tests carried out were overcharge and overdischarge. For the overcharge test, the flow battery was taken to a full charge of 1.7 V with a 1.0 A current and continued into an overcharge condition for another 6 hours. For the overdischarge test, the flow battery was subjected to a load of 1 A to remove an additional 150% of the original capacity after the cell reached 0 V.

The commercial large-scale zinc/bromine redox flow battery was procured from Redflow Ltd. The battery was a 60 V 200 Ah system. A photo of the test article is shown in Figure 4.

The battery has an integrated module management system (MMS) that provides protection against several off-nominal conditions. The MMS provides protection against overvoltage, undervoltage, overtemperature, and overcurrent (short circuits) and also shuts down in the event

of electrolyte leakage and gas evolution. The off-nominal tests on this battery were carried out with the MMS bypassed and connecting directly to the cell terminals in order to subject the module to the off-nominal condition without the MMS interception. This was the only way worst-case results could be determined in the event of an off-nominal condition and failure of MMS protections.
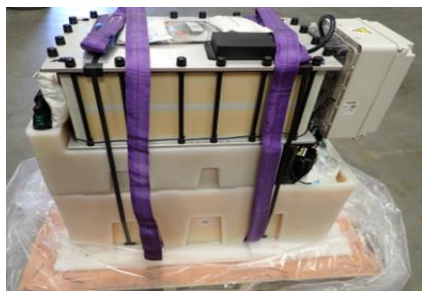

Figure 4. Commercial-scale Zn/Br_2 redox flow battery.

The overcharge was carried out by charging the module with a current of 45 A to a limit of 100 V or for a total capacity of 600 Ah. The overdischarge was carried out initially by taking the battery down to 0 V and then removing 150% of additional capacity. However, the current steadily fell from 30 A to 0.5 A with the voltage going from -3 V to greater than 0 V. The test was therefore carried out by holding it at ~ 500 mV for a period of almost 24 hours. The external short circuit was carried out with a load of 20 mohms for a total of three hours. Voltage, current, and temperatures were monitored during the entire test period. Gas sensors from MSA were used to monitor oxygen, carbon dioxide, hydrogen, and bromine gas.

Results and Discussion

Vanadium Flow Battery

The vanadium lab scale flow battery was subjected to overcharge and overdischarge tests only. The overcharge test resulted in excessive gas production in both the catholyte and anolyte and the graphite plates in the flow battery cell on the side of the cathode showed severe degradation while the anode side appeared very clean, as shown in Figure 5. However, bubbling inside the Erlenmeyer flasks was observed only in the case of the catholyte while the gas production in the anolyte was mainly observed by the presence of significant gas bubble production in the tubes, shown in Figure 6. The voltage and temperature data are shown in Figure 7 for the overcharge test.

The overdischarge test did not result in any significant gas production. The voltage and temperature data for the overdischarge test is shown in Figure 8. No degradation of either of the electrodes or flow channels was observed.
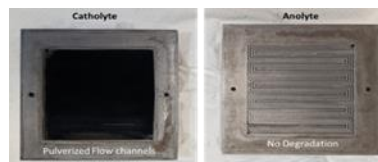

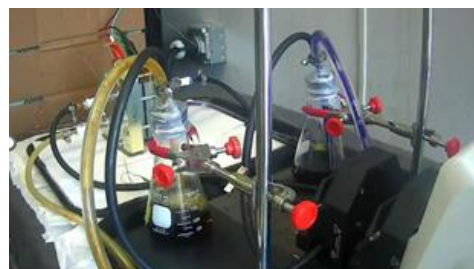Figure 5. Vanadium flow battery cell showing the electrolyte flow channels on both electrodes.

Figure 6. Overcharge test showing bubbling in the catholyte flask.
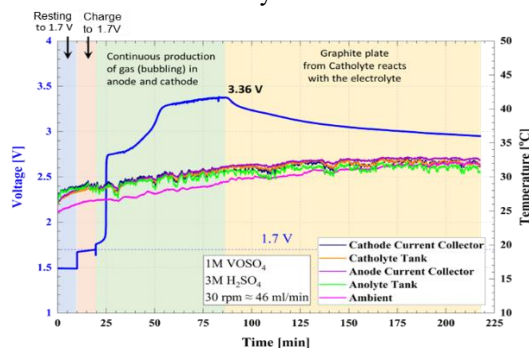

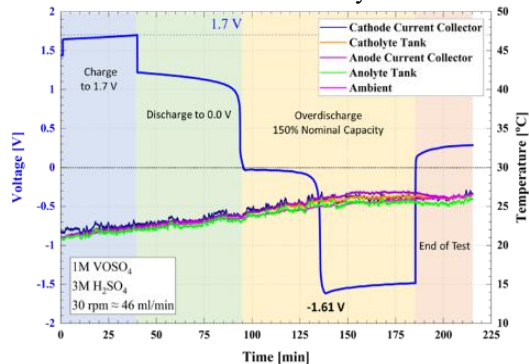Figure 7. Voltage and temperature plots for the overcharge test of the vanadium system.

Figure 8. Plot of voltage and temperature for the overdischarge test of the vanadium system.

Zinc – Bromine Flow Battery

The overcharge test of the Zn/Br_2 system caused the release of bromine gas from the electrolyte tank. The measured gas concentration was >5 ppm at 9 inches from the pressure relief vent. A review of the electrochemical equations shows that bromine gas is released during the charge process and the MEP is used to sequester gaseous bromine and keep it in solution. However, when there is excessive bromine gas

released, the quantity of MEP in the system is not sufficient for the sequestration causing the gas to be released through the vents. It is not clear if hydrogen gas was evolved since the excess bromine release may have masked any evolved hydrogen gas. A maximum temperature of 83 °C was recorded in the zinc (catholyte) tank. Figure 9 shows the voltage, current, and temperature of the RFB during the overcharge test. The zinc tank displayed a temporary deformation at the end of the overcharge test.
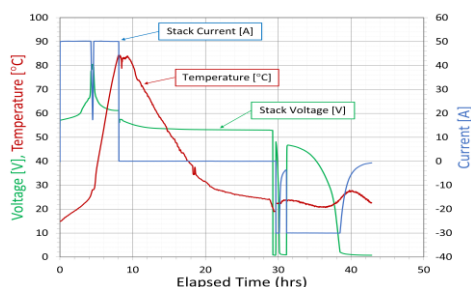

Figure 9. Plots of voltage, current, and temperature for the overcharge test of the Zn/Br$_2$ RFB.

The overdischarge test did not show any excessive gas production or high temperatures. The external short test caused the voltage of the battery to fall to 0 V before the 3 hour hold and the maximum temperature observed was less than 80 °C, as shown in Figure 10.
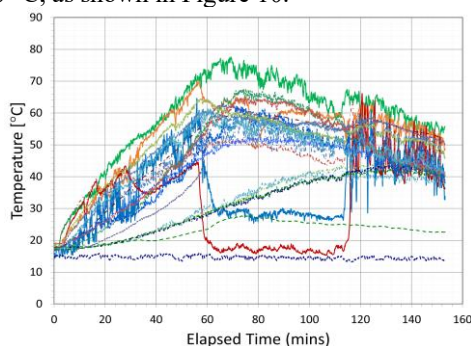

Figure 10. Temperature trends during the external short test.

Conclusions

The two flow battery chemistries studied in this work indicate that a good characterization and understanding of the system as a whole is required to determine the worst-case results of an off-nominal condition. Gas production in both systems indicate that if the controls are not set in the relevant manner, combustible and toxic gases can be released into the environment. The test articles should be tested under off-nominal conditions to fully understand the worst-case behavior before safety limits are set into the module and battery management systems.

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