

## INVESTIGATING IMPROVEMENTS ON REDOX FLOW BATTERIES CSIR/MSM/EP/EXP/2006/0099/A

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### Abstract

As fossil fuel resources become depleted and concerns about global warming increases, focus on renewable energy sources will become more urgent. The problem however is the intermittent nature of these sources, which necessitates the need for energy storage devices coupled to most of their applications. Lead-acid batteries have long been used as the most economical option to store electricity in many small scale applications, but lately more interest have been shown in redox flow batteries. The low power densities of redox flow batteries however limit their application to large-scale storage and mostly stationary use, while costs still favour lead-acid batteries.

Studies done at the CSIR have identified possible redox couples that could be used in a redox flow battery that not only reduces the costs significantly, but would also improve the power densities of the battery itself, thus broadening the market applications for redox flow batteries.

Preliminary results thus far have indicated that these new couples could provide a battery that competes well with the current commercially available redox flow batteries. Further testing is still underway to optimise the battery parameters, determine battery lifetime as well as determining the efficiencies during long cycling.

### Keywords

Redox flow, bromine, vanadium, storage, battery

### Introduction

With the increased pressure on fossil fuel reserves and concerns about global warming, renewable energy sources are receiving increased attention. However, the intermittent nature of these sources makes them unreliable especially for off-grid applications. Redox flow batteries provide a means to bridge the time lag between the availability of renewable energy and the time when it is needed, and thus provide a more sustained energy output.

Applications for redox flow batteries include the following:

- *Telecommunications*: exchange sites, data centers
- *Non-grid connected applications*: remote communities, hospitals and schools, solar photovoltaic and other renewable energy
- *Grid connected applications*: Uninterrupted Power Supply (UPS), load levelling

A redox flow battery comprises the following components:

- anode
- cathode
- electrolytes (anolyte and catholyte)

- current collectors (electrodes)
- porous separator (membrane)

As can be seen, it does not differ greatly from more conventional batteries, in terms of construction. The main difference between a redox flow battery and conventional batteries is that the reactants stay in solution in both the charged and discharged state. Electrodes in a redox flow battery are thus inert and act merely as current collectors, whereas they are the active components in a conventional battery. This has the added advantage of decoupling the capacity and power rating in redox flow batteries; thus a large capacity, high power battery can readily be produced as used for load levelling purposes.

One disadvantage of redox flow batteries however is the low energy densities (Wh/kg) as compared with other available energy storage applications. This limits the applications of redox flow batteries to mostly stationary applications. In an attempt to increase the energy density of the system, a number of redox couples have been investigated and reported on.

Commercially available redox flow batteries include the zinc-bromine (Zn-Br) battery (a pseudo redox flow battery) as well as the all-vanadium (V-V) battery. Although these batteries provide efficiencies greater than or equal to those of lead-acid batteries, further improvements are still desired. Firstly, the Zn-Br battery could suffer from efficiency losses due to uneven zinc deposition on the electrodes at high charge rates. Secondly, the cost of the V-V battery is high due to the expensive reagents used.

Various authors (Kaneko et al (1994), Skyllas-Kazacos (2003), Vafiados et al (2006)) have tried to find a cheaper source of vanadium and thus reducing the overall costs. A novel battery opportunity existed by investigating a combination of the Zn-Br and V-V battery. By using a bromine/bromide couple in the positive half-cell of the battery, the overall costs of the V-V battery could be reduced by as much as 40%. Also, because of the higher solubility of the bromide, the energy density of such a battery is higher than the V-V battery.

The battery still uses a vanadium reagent in the negative half-cell of the battery which is expensive. A further alternative to the V-Br battery by replacing the vanadium with chrome is also discussed herein.

The main objectives of this study were to investigate alternatives to the currently available redox flow batteries. Once suitable couples have been identified, their performance will be tested in a lab-scale redox flow battery. Improvements to the performance of the tested cell will be conducted by identifying key parameters and investigating their effects on the performance of the cell.

## Experimental

An experimental cell was constructed according to Figure 1 below:

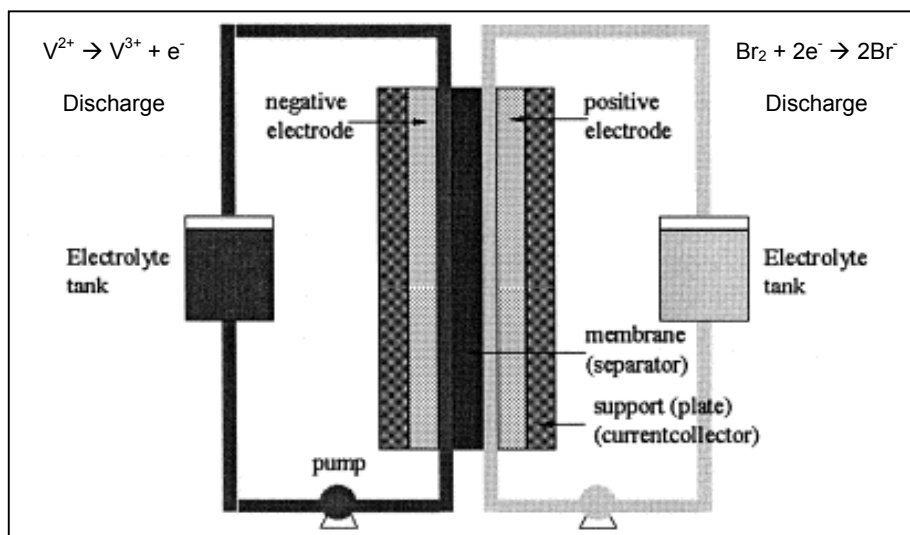


Figure 1: Schematic of cell construction

The cell employed a graphite felt electrode (5cm x 7cm x 0.3cm) in each half-cell and a current collector. The current collectors tested were aluminium, copper or platinum. Peristaltic pumps circulated the electrolyte through the cell via flow frames containing the graphite electrodes. A membrane separator was placed between the two flow frames to separate each half-cell. Rubber gaskets were placed between cell components to prevent leakages (in some cases silicone sealant was applied for the same reason). Two PVC end plates were bolted together to tighten and seal the cell components.

The cell was operated under the following conditions:

Table 1: Initial cell operating parameters

$[V^{3+}]$	<b>1M</b>
$[Br]$	<b>2M</b>
Electrode Area	35 cm <sup>2</sup>
Flowrate	70 ml/min
Electrode material	Graphite felt
Membrane	Selemon AMV (anion exchange membrane)
Support electrolyte	<b>2M</b> H <sub>2</sub> SO <sub>4</sub>

Because of the instability of  $V^{2+}$  in oxygen/air, nitrogen was sparged into the reservoir to provide an inert atmosphere.

Discharge curves were obtained by drawing currents through appropriate external resistors of varying values ranging from 1 – 100  $\Omega$  for approximately 3 minutes and recording the voltage and amperage at the end of the 3 minute periods. In most cases the observed potential and current stabilised after 2 minutes. The current was read with a digital multimeter.

## Results

Initial tests set to proof that a V-Br redox flow battery could be feasible as an alternative to the V-V redox flow battery. The initial proof of concept results are given in Figure 2, where it can be seen that an average of 1.3V was obtained.

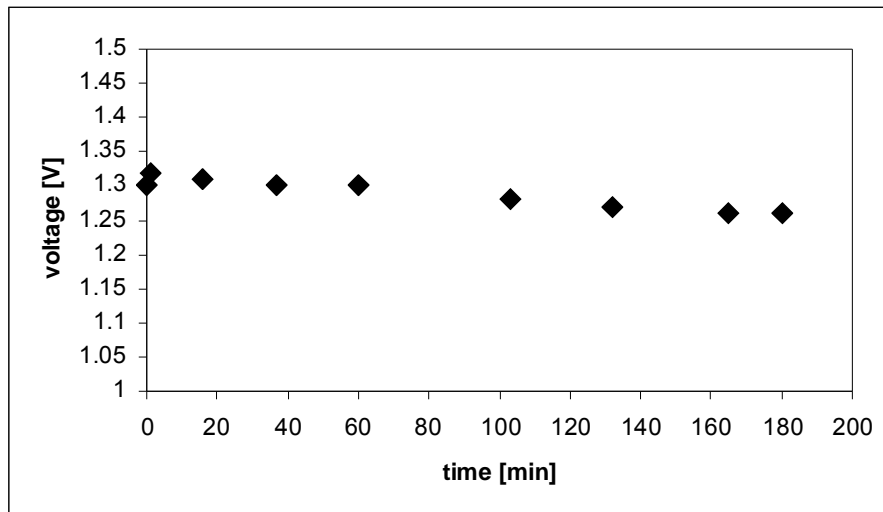


Figure 2: Open-circuit voltage of V-Br battery – initial proof of concept

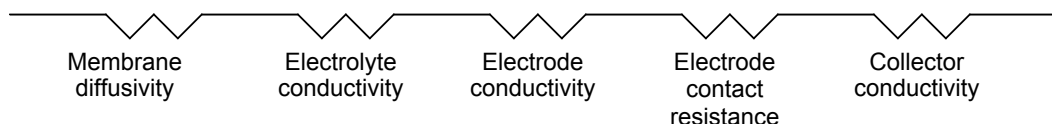
The reactions involved are:



The theoretical voltage for the V-Br battery under standard conditions is 1.32V. The initial results thus showed that a redox flow battery using this couple could be a suitable replacement to the V-V battery (theoretical voltage = 1.26V). Although the open-circuit (OC) voltage merely indicates the potential of the active couple, the battery would still have to be tested under various loads, plus continuous cell charge-discharge cycling.

No charge-discharge curves are presented here because of many operational issues experienced during the test cycling. One of the problems identified during these cycles however, was the high internal resistance of the battery and these were addressed by identifying the key parameters that could decrease this resistance.

The internal resistance of the battery can be visualised with the following schematic that illustrates each resistance encountered for current flow in each half-cell:



Each component of the redox flow battery thus has a significant potential impact on the internal resistance of the battery and each one would have to be optimised individually. The discussions that follow here forth are based only on the effect that the current collectors have on battery characteristics.

In the first tests, copper current collectors were employed. The collectors were placed against a carbon paper sheet that prevented it from coming into contact with the corrosive electrolyte, but still made contact with the electrodes. The results for the copper current collectors are given in Figure 3. The low current density could at first not be explained, but when the cell was opened, it was noted that a large percentage of the copper was covered by a non-conductive substance.

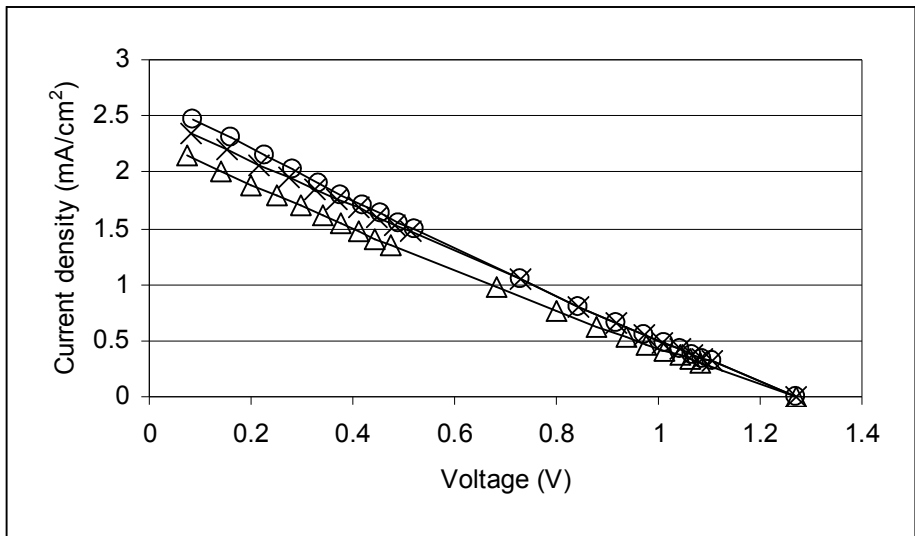


Figure 3: Current density vs. voltage curves when using Cu collectors (high resistance)

The effect of this non-conductive layer increased the overall resistance of the cell and thus resulted in a lower current output. This effect was also noticed on the dc power supply when the same charging current was used. On “fresh” copper, the voltage reading (during constant current charge) on the power supply was nearly half of that on the coated copper. Thus a better method for protecting the current collector needs to be investigated. Currently, the use of a carbon sheet/plate is being tested that fits between the collector and the electrode but still provides adequate conductivity.

Following on from the copper trials, aluminium was also tested as an alternative current collector. In a similar manner, the aluminium was not allowed to come into contact with the electrolyte, by placing a graphite paper/foil between the collector and the electrode. The marked increase of using this collector in this combination is shown in Figure 4. Also given in Figure 4 are the results when using a platinum collector.

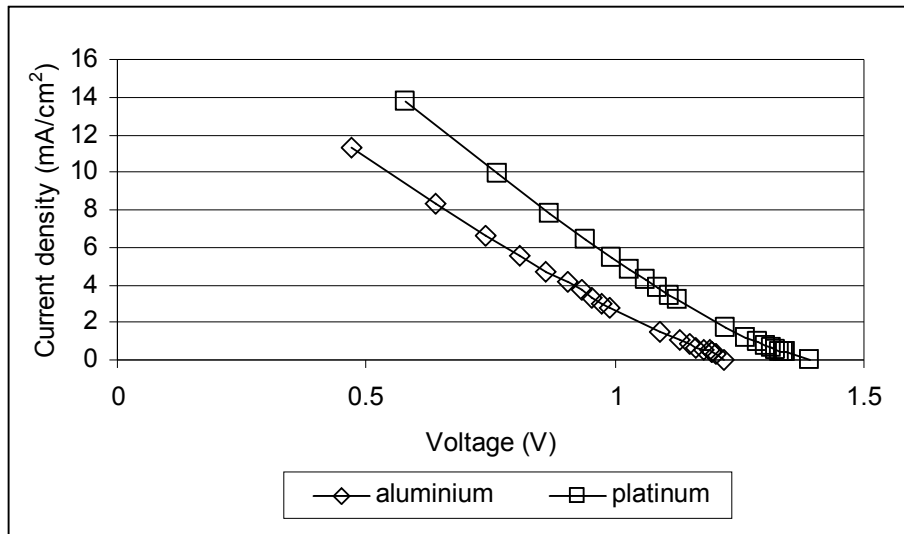


Figure 4: Current density vs. voltage curves when using Al and Pt collectors

When the cell was again opened to investigate the condition of the aluminium collector, it was noted that some pitting had occurred, thus indicating that electrolyte had leaked onto the collector. Similar to the copper, more tests are being conducted by using a carbon sheet/plate to minimise contact between the collector and the electrolyte.

This problem was not noted when using platinum, largely because of platinum being inert to the corrosive electrolyte. Platinum current collectors are not economical, but were used to set a bench-mark with regard to minimising any resistance that can be built up by corrosion products or other types of metals. Platinum also tends to favour hydrogen formation, and should the electrolyte come into contact with the collector, this would result in Coulombic losses as well as being potentially hazardous.

It should be noted that even though only one factor was addressed, all the other factors play a combined role in increasing the current density of the battery. An improved battery design, which should have a reduced internal resistance, is currently being investigated. At the time of writing this paper, no results were available.

Figure 5 shows the power densities measured when using the three alternative current collector materials. Platinum is significantly better than the others in terms of power density achieved. A maximum of  $8\text{mW/cm}^2$  was obtained at  $0.6\text{V}$  using the Pt collectors.

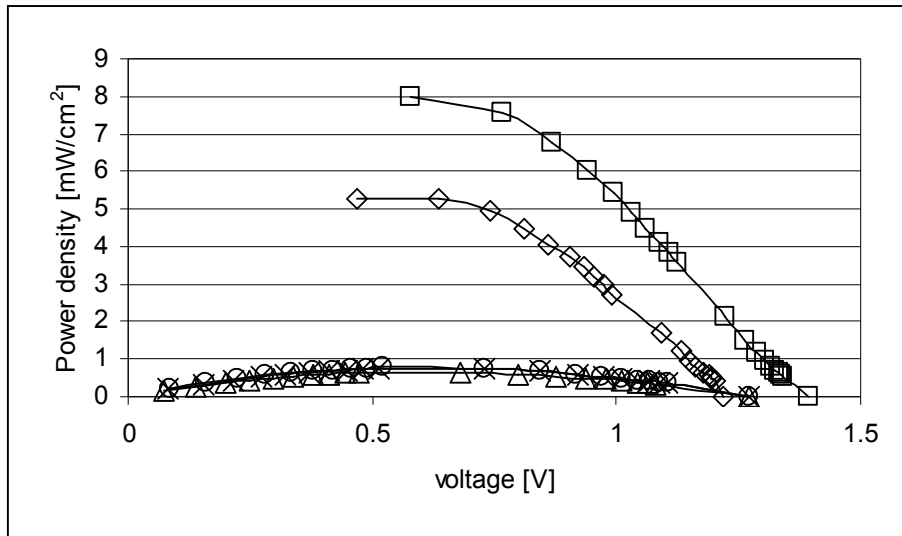


Figure 5: Power density vs. voltage (Current collectors:  $\diamond$  - Al;  $\square$  - Pt;  $\Delta$ ,  $\circ$ ,  $\times$  - Cu)

In an attempt to further reduce the cost of a redox flow battery, the use of cheaper alternative couples has been investigated. An attractive alternative is a Cr-Br battery. Development of this battery is still at a proof of concept stage and only preliminary results are available.

Figure 6 shows the open-circuit voltage for this battery, achieving an average open-circuit voltage of 1.44V. The theoretical standard voltage for such a couple is 1.49V.

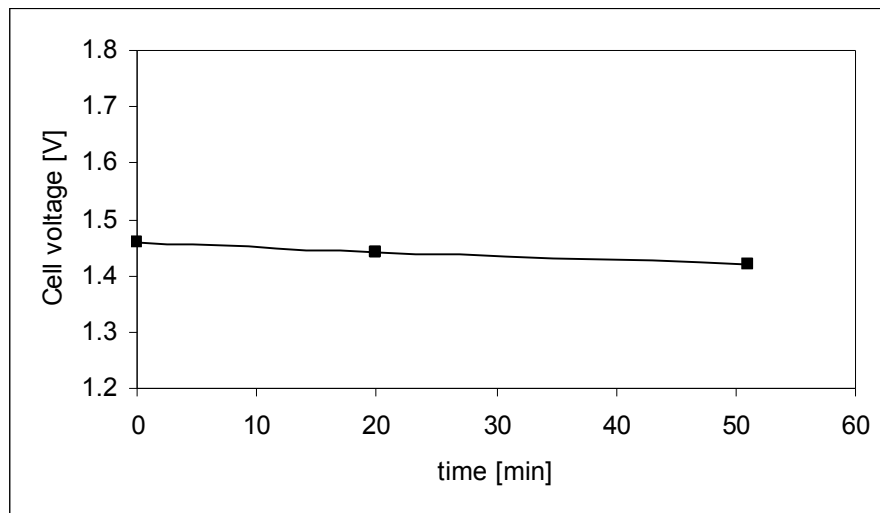


Figure 6: Open-circuit voltage of a Cr-Br battery

The OC voltage highlights the potential of this system as an alternative to the V-V as well as V-Br battery. Tests are currently underway to determine the efficiencies of these batteries and these will be used to compare against the available redox flow batteries. Assuming that this battery has the same efficiencies as the V-V battery, the cost of reagents for such a battery could be as much as 80% cheaper (numbers based on lab chemical process).

Table 2 below gives a theoretical comparison of the Coulombic storage densities and the energy densities of the different batteries mentioned in this report. The V-Br and Cr-Br batteries have energy densities more than double that of the current V-V battery.

Table 2: Theoretical battery comparisons

Battery	V-V	V-Br	Cr-Br
Ah/kg	19	38	38
Wh/kg	24	50	57

One of the major obstacles that would have to be overcome when using mixed electrolytes is the cross-contamination of the species across the membrane. In the case of the V-V battery, this cross-contamination is negated because of the use of the same species on both sides. Cross contamination directly results in a loss of efficiency.

For the V-Br and Cr-Br batteries to be competitive in the market, it would have to give similar efficiencies to that of the vanadium battery, thus providing a battery of the same functionality, but at a significantly reduced cost.

## Conclusions

While research is still continuing on the redox flow batteries, preliminary results have indicated that potential for improvement exists to develop a redox flow battery that is cheaper to manufacture than the commercial V-V battery. Cell and battery optimisation is currently underway to produce a battery that has low internal resistance and thus favourable voltage and current efficiencies. Once this optimisation is complete, the battery should be subjected to continuous charge-discharge cycles so as to complete a thorough comparison with other available technologies.

## References

Kaneko, H, Negishi, A, Nozaki, K, Sato, K, Nakajima, M, "Redox battery", US Patent 5318865, 1994

Skyllas-Kazacos, M, "Novel vanadium chloride/polyhalide redox flow battery", Journal of Power Sources, 124 (2003), 299 – 302

Vafiadis, H and Skyllas-Kazacos, M, "Evaluation of membranes for the novel vanadium bromine redox flow battery", Journal of Membrane Science (2006) – article in press