

## Recent advances with UNSW vanadium-based redox flow batteries

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### SUMMARY

The vanadium redox flow battery pioneered by Skyllas-Kazacos *et al.* at the University of New South Wales (UNSW) is currently considered as one of the few electrochemical energy storage systems suitable for use in the large-scale utility applications that are emerging in response to the increasing global implementation of renewable energy technologies for the mitigation of greenhouse gas emissions. While the original all-vanadium redox flow battery (G1 VRF) has already been successfully implemented in a wide range of stationary field trials in Japan, U.S.A., Austria, Italy and Australia, further cost reduction has been needed for its widespread market up-take. In this paper, up to 80% efficiency is reported for the latest 5–10 kW G1 VRF battery stack employing low-cost stack materials that are expected to achieve the necessary cost structure for the majority of stationary energy storage applications. While the G1 VRF battery has shown high efficiencies and excellent cycle life, however, its low energy density has restricted its use in mobile applications. The new Generation 2 vanadium bromide redox battery (G2 V/Br) patented by UNSW in 2001 has been shown to potentially double the energy density of the G1 VRF battery, allowing mobile applications to be considered. In this paper, the performance of the G2 V/Br is presented at a range of temperatures and the use of complexing agents is shown to successfully bind any bromine produced during charging to prevent the formation of bromine vapours. Copyright © 2009 John Wiley & Sons, Ltd.

KEY WORDS: energy storage

### 1. INTRODUCTION

The redox flow cell or battery is an electrochemical system that stores energy in two solutions containing different redox couples. Unlike conventional batteries, the system power and capacity can be independently varied by adjusting the size of the cell stack and the electrolyte volumes. The redox

flow cell is therefore more like a rechargeable fuel cell than a battery. The earliest work on the redox flow cell was undertaken at NSA's Lawrence Laboratories by Thaller in the early to mid 1970s [1, 2]. Since then, several other systems have been proposed, but the vanadium redox battery pioneered at the University of New South Wales (UNSW) has shown the greatest potential for

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large-scale energy storage applications with long cycle life and high energy efficiencies of over 80% in large installations. The original all-vanadium redox flow battery (G1 VRF) employs the V(III)/V(II) and V(V)/V(IV) redox couples in sulphuric acid as the negative and positive half-cell electrolytes, respectively [3–8]. Having the same element in both half-cells, it overcomes the problem of cross contamination caused by the transfer of ions across the membrane.

In spite of its significant advantages in terms of performance and cycle life, the G1 VRF has a relatively low energy density that restricts its use in certain applications that have space or weight restrictions. The G2 V/Br patented by the UNSW overcomes this limitation while still using the same elements in both half-cell electrolytes. In this paper, recent progress in the area of cost reduction of the G1 VRF battery and optimization of the G2 V/Br is presented.

## 2. GENERATION 1 ALL-VANADIUM REDOX FLOW BATTERY

More than 20 VRF battery demonstration systems covering a wide range of applications have already been completed in Japan, Europe and the U.S.A., a selection of which is listed below [9]:

1. 200 kW/800 kWh installed by Mitsubishi Chemicals (1996) at Kashima-Kita Electric Power, Japan for load-levelling [10].
2. 450 kW/900 kWh installed by Sumitomo Electric Industries (SEI) (1996) at Tasumi Sub-Station, Kansai Electric, Japan, for peak shaving.
3. 200 kW/1.6 MWh installed by SEI (2000) at Kansai Electric, Japan for peak shaving.
4. 170/1 MW installed by SEI (2001) at Hokkaido Electric Power Wind farm, Japan for wind turbine output power stabilization.
5. 1.5 MW/1.5 MWh installed by SEI (2001) at Tottori Sanyo Electric, Japan for peak shaving and emergency back-up power [11].
6. 250 kW/500 kWh installed by VRB Power (2001) at Stellenbosch University for ESKOM Power Corporation, South Africa for peak shaving and UPS back-up power.

7. 500 kW/5 MWh installed by SEI in 2001 at Gwansei Gakuin University Japan for peak shaving.
8. 42 kW/90 kWh installed by SEI in 2001 at CESI, Milan, Italy for R&D into distributed power systems.
9. 500 kW/2 MWh installed by SEI in 2003 in High-Tech factory in Japan for UPS/peak shaving [11].
10. 250 kW/1 MMWh installed by Pinnacle VRB in 2003 for Hydro Tasmania on King Island for wind energy storage and diesel fuel replacement [12].
11. 250 kW/2 MWh installed for PacificCorp by VRB Power in 2004 in Moab, Utah, U.S.A. for voltage support, rural feeder augmentation [13].
12. 4 MW/6 MWh installed by SEI in 2005 for J Power at Subaru Wind Farm, Tomahae, Hokkaido, Japan for wind energy storage and wind power stabilization [14].

To date, most of the field trials and demonstrations of the G1 VRF battery have been completed by SEI (Japan), with the largest being a 4 MW/6 MWh VRF battery system installed at the Subaru windfarm on the Japanese island of Hokkaido. With each of these demonstrations, overall round-trip energy efficiencies up to 80% have been reported and a cycle life of over 12 000 cycles was achieved with 20 kW stack modules by SEI [15].

Although the VRF battery has shown excellent performance and technical capabilities for a wide range of applications, further cost reduction is needed to allow it to reach full-scale commercial fruition. As the most expensive component is the membrane, further work has been undertaken by a number of laboratories in recent years [16–20], to develop low-cost alternatives to the original membranes used by the UNSW group [21–23], SEI [24], and VRB Power [25]. In spite of this, however, expensive Nafion membrane has still been employed in many G1 VRF battery demonstrations [25,26]. A large screening programme was undertaken by V-Fuel between 2005 and 2007 and several new membranes were identified as potential low-cost candidates. One of these, with a cost of less than one-third that of Nafion 112, was subjected to extensive chemical modification trials to

enhance its electrochemical performance and the modified membrane was subsequently evaluated in the 5–10 kW stack illustrated in Figure 1.

The general specifications of the V-Fuel 5–10 kW stack were as follows:

Electrode Area: 1500 cm<sup>2</sup>

Number of Cells: 40

Bipolar electrodes: 3–4 mm thick carbon felt bonded onto conducting plastic substrates

Membrane type: cation exchange, VF11 (V-Fuel Pty Ltd, Sydney)

This stack was subjected to charge–discharge cycling using a constant charging current of 30 A up to a cell voltage limit of 1.8 V, while discharge was performed at a range of currents between 30 and 200 A. The electrolyte used comprised 1.7 M Vanadium in H<sub>2</sub>SO<sub>4</sub>.

Figure 2 shows the discharge curves obtained at each current while the stack efficiencies and capacity as a function of discharge current are presented in Figure 3. It should be mentioned that the discharge time on the *X*-axis are shown in arbitrary units since this is a function of electrolyte volume and can be independently varied to suit specific user requirements.

As seen in Figure 3, the coulombic efficiency is seen to increase to a maximum value of 91% at a discharge current of 120 A (80 mA cm<sup>-2</sup>) before declining to 86% at 200 A discharge (133 mA cm<sup>-2</sup>). This trend in coulombic efficiency is caused by the self-discharge across the membrane at the lower current (corresponding to longer times), while at the

higher current, the drop in voltage due to concentration overvoltage effects gives rise to a slightly premature cut-off in the discharge process as is also evident by the slight drop in capacity at that current. In contrast, the voltage efficiency shows a monotonic decrease with increasing current due to higher ohmic (*iR*) losses at the higher currents. By multiplying the coulombic efficiency and voltage efficiency at each current, the overall energy efficiency is calculated and the results are also plotted in Figure 3. An energy efficiency of 80% is thus obtained at discharge currents of 50–60 A (33–40 mA cm<sup>-2</sup>), while the capacity remains relatively constant up to 120 A, with a slight decline observed at 200 A, as discussed above.

While these results show excellent performance for use in most large-scale energy storage applications, the low energy density of the G1 VRF battery limits its use to stationary systems. In an effort to

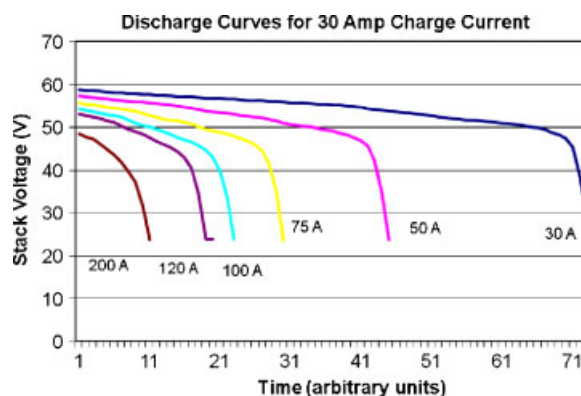


Figure 2. Discharge curves at various currents for charge current of 30 A.

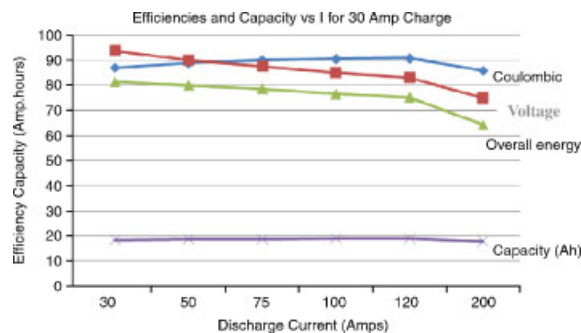


Figure 3. Stack efficiencies and capacity versus stack discharge current (note discontinuity between 120 and 200 A).

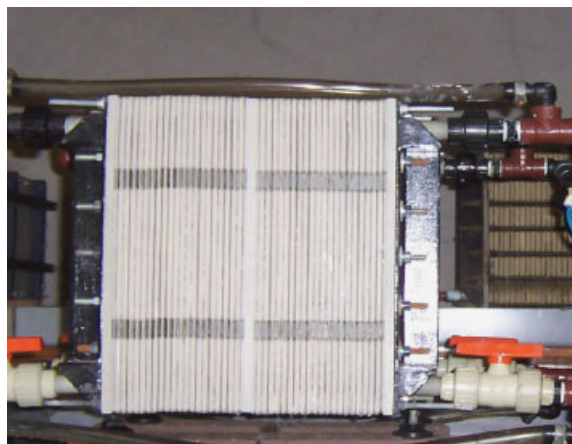


Figure 1. V-Fuel's 5–10 kW G1 VRF battery stack.

enhance the energy density of the G1 VRF battery for potential application in mobile systems, further work was conducted at UNSW in early 2000 to identify alternative supporting electrolytes that allow higher solubility of the vanadium couples.

### 3. GENERATION 2 V/BR REDOX FLOW BATTERY

While G1 VRF battery employs a solution of vanadium sulphate in sulphuric acid on both sides, the G2 V/Br employs a vanadium bromide solution in both half-cells [27, 28]. A comparison of the G1 and G2 technologies is provided in Table I. The higher solubility of vanadium bromide allows energy density to be almost doubled (to around 50 Wh kg<sup>-1</sup>). The higher solubility of vanadium bromide also allows lower-temperature operation compared with the G1 VRF battery system.

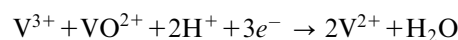
Typically, the G2 V/Br electrolyte includes 7–9 M HBr plus 1.5–2 M HCl. By utilizing more of the available bromide ions in the positive half-cell during charging, the volume of the positive half-cell electrolyte reservoir can be almost halved, thereby reducing the total electrolyte volume by almost 25% and further increasing the energy density of the V/Br cell. The initial challenge for the G2 V/Br was to identify low cost, long-life, high-performance carbon felt and membrane materials for the cell stack and a wide range of candidates was evaluated by UNSW and V-Fuel.

#### 3.1. Preliminary studies with 2 M vanadium bromide electrolyte

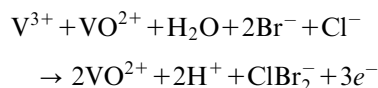
The VF11 membrane was selected for charge–discharge performance studies in a 2.6 M

vanadium bromide electrolyte over a range of temperatures and current densities. These studies employed a small laboratory scale cell with electrode area of 25 cm<sup>2</sup>, carbon felt electrodes (Fibre Materials Inc, U.S.A.) and graphite board current collectors (ABTT Ltd., Australia). The electrolyte used comprised 2.6 M vanadium ions in 7.5 M HBr plus 1.5 M HCl and 65 ml of a 50:50 V(III):V(IV) mixture (abbreviated as V<sup>3.5+</sup> was used as the initial electrolyte in each half-cell.

During the initial charge, the V(III) and V(IV) ions are reduced to V<sup>2+</sup> in the negative half-cell according to the reaction:



while in the positive half-cell, the initial two-step charge reaction involves oxidation of V<sup>3+</sup> to VO<sup>2+</sup> in the first step followed by oxidation of the halide ions to ClBr<sub>2</sub><sup>-</sup> according to:



Subsequent charge–discharge cycling involves the V<sup>2+</sup>/V<sup>3+</sup> couple and ClBr<sub>2</sub><sup>-</sup>/Br<sup>-</sup> couple in the negative and positive half-cells respectively.

Figure 4 shows a typical series of charge–discharge curves obtained at 30°C using a charge–discharge current density of 20 mA cm<sup>-2</sup>.

From these and other tests conducted at different current densities, the cell efficiencies were determined at a range of temperatures. Figures 4–6 present the variation in coulombic, voltage and overall energy efficiency, respectively, as a function of charge–discharge current density for temperatures of 10, 20, 30 and 40°C.

These results show that overall energy efficiencies of around 70% can be obtained at a current density of 20 mA cm<sup>-2</sup> and temperatures of 10, 20 and 30°C. As expected, voltage efficiency decreases with decreasing temperature and increasing current temperature due to lower reaction rates and increasing iR losses, respectively. On the other hand, coulombic efficiency generally increases with increasing current density due to lower self-discharge across the membrane at shorter charge–discharge times. The coulombic efficiency also decreases with increasing temperature

Table I. Comparison between G1 VRF and G2 V/Br.

	G1 VRF	G2 V/Br
Electrolyte	1.5–2 M V/Sulphate in both half-cells	2–3 M V/Br in both half-cells
Negative couple	V <sup>3+</sup> /V <sup>2+</sup>	V <sup>3+</sup> /V <sup>2+</sup>
Positive couple	V(IV)/V(V)	Br <sup>-</sup> /Br <sub>3</sub> <sup>-</sup>
Specific Energy (energy kg <sup>-1</sup> )	15–25 Wh kg <sup>-1</sup>	25–50 Wh kg <sup>-1</sup>
Energy density (energy l <sup>-1</sup> )	20–33 Wh l <sup>-1</sup>	35–70 Wh l <sup>-1</sup>

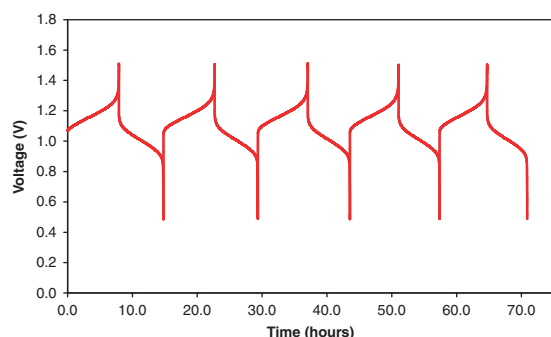


Figure 4. Typical charge-discharge curves for V/Br cell employing 2.6 M vanadium bromide electrolyte. Charge-discharge current density =  $20 \text{ mA cm}^{-2}$ ,  $T = 30^\circ\text{C}$ .

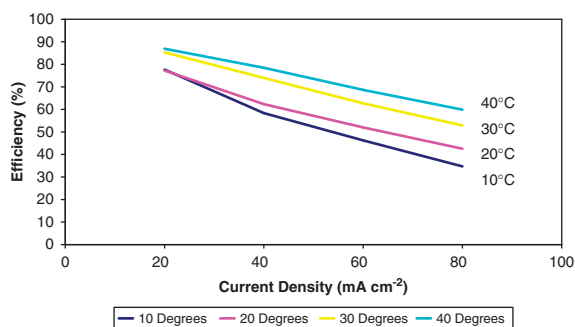


Figure 5. Voltage efficiency versus current and temperature for cell employing 2.6 M V electrolyte in 7.5 M HBr plus 1.5 M HCl.

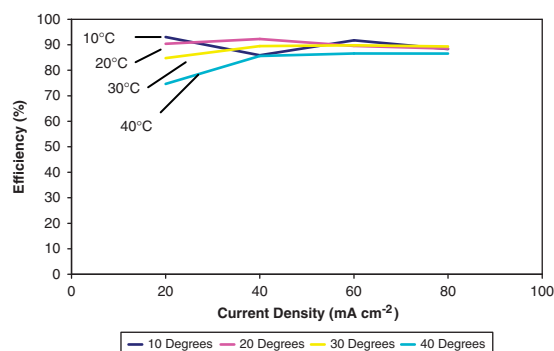


Figure 6. Coulombic efficiency versus current and temperature for cell of Figure 5.

as a result of faster diffusion rates of vanadium and polybromide ions across the membrane at elevated temperatures.

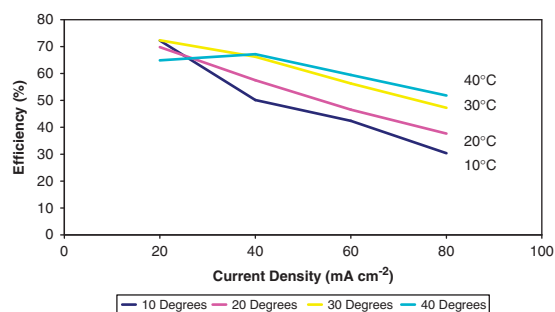


Figure 7. Overall energy efficiency versus current and temperature for cell of Figure 5.

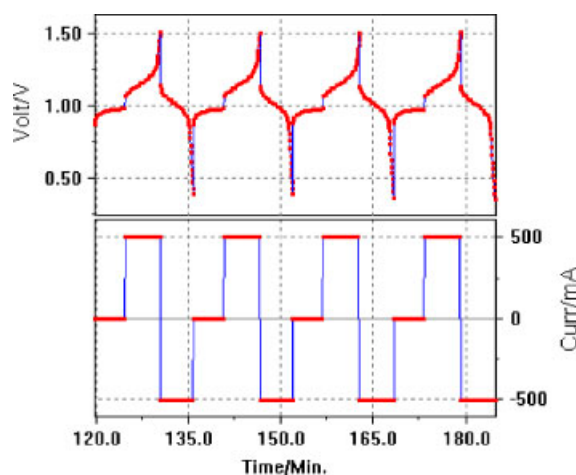


Figure 8. Charge-discharge curves obtained for small static cell employing VF carbon felt, VF11 membrane and 2 M vanadium electrolyte in 7 M HBr plus 2 M HCl.

### 3.2. Electrode screening studies

Further optimization of the G2 V/Br cell was undertaken by extensive screening of carbon and graphite felt electrode materials. These screening studies were carried out in a small static test cell without external reservoirs and pumps. The cell employed the VF11 membrane and the electrode area was  $25 \text{ cm}^2$ .

Figure 7 shows typical charge-discharge curves for the cell employing the 2 M V/Br electrolyte. Two pieces of each carbon felt sample were first soaked in the electrolyte and then inserted into the static cell before charge-discharge cycling at a current density of  $20 \text{ mA cm}^{-2}$ . Several carbon and graphite felts were tested from a range of suppliers, and the best performance obtained is illustrated in Figure 8.

From these results, average voltage and coulombic efficiencies of 87 and 92% were calculated, giving an overall energy efficiency of 80% at  $25 \text{ mA cm}^{-2}$  charge and discharge currents. These results confirm that higher energy efficiencies can be obtained with optimized cell design and cell materials.

### 3.3. Bromine complexing agents

A potential concern over the G2 V/Br cell is the possibility of bromine vapour emissions during operation. To overcome this potential hazard, the use of bromine complexing agents has been studied. A range of bromine complexing agents including tetrabutylammonium bromide, polyethylene glycol, *N*-methyl-*N*-ethyl morpholinium bromide and *N*-methyl-*N*-ethyl pyrrolidinium bromide, was evaluated to determine their effectiveness in binding any bromine produced in the positive half-cell during the charging reaction to prevent bromine vapour emission. These and other complexing agents were added in different ratios to an approximately 3 M V(IV) solution containing 1.5 M Br<sub>2</sub> in 8 M HBr and 2 M HCl and the stability of the solutions was examined at different temperatures.

Results obtained with mixtures of two complexing agents (proprietary) at a Br<sub>2</sub> to total complexing agent molar ratio of 2:1 are presented in Table II.

Although the corresponding electrolyte without any complexing agent showed a significant amount of brown bromine vapour above the solution at each temperature, these results demonstrate that the addition of 0.75–0.8 M total complexing agent can effectively eliminate bromine vapour at a temperature of 11°C, with all of the bromine effectively bound as an orange oily layer that settles to the bottom of the sample bottles. At 25°C, Solutions 2, 5 and 6 show no vapour formation; however, on increasing the temperature to 40°C, a small amount of brown vapour is observed in all containers with the exception of Solution 6.

Although the chemical composition of the orange oily layer has yet to be confirmed, the fact that it is only formed in the presence of both Br<sub>2</sub> and the complexing agents (both in the presence and absence of any vanadium ions), indicates that it must be a bromine compound as has also been reported for the Zn/Br battery [29, 30]. Further studies of the bromine complexing agents are

Table II. Effect of Br<sub>2</sub> complexing agents on vanadium electrolyte appearance.

Sample number	Solution composition	11°C for 10 days	25°C for 15 days	40°C for 10 day
1	3 M V(IV) 1.5 M Br <sub>2</sub> 0.75 M 'A'	Dark green liquid with orange liquid organic layer	Dark green aqueous layer with some brown gas and orange organic liquid layer	N/A
2	3 M V(IV) 1.5 M Br <sub>2</sub> 0.5 M 'A' 0.25 M 'B'	Dark green liquid with orange layer	Dark green liquid with orange layer	Dark green liquid with some brown gas and orange layer
3	3 M V(IV) 1.5 M Br <sub>2</sub> 0.38 M 'A' 0.38 M 'B'	Dark green liquid with orange liquid organic layer	Dark green liquid with some brown gas and orange liquid organic layer	N/A
4	3 M V(IV) 1.5 M Br <sub>2</sub> 0.25 M 'A' 0.5 M 'B'	Dark green liquid with orange liquid organic layer	Dark green liquid with some brown gas and orange liquid organic layer	N/A
5	3 M V(IV) 1.5 M Br <sub>2</sub> 0.20 M 'A' 0.6 M 'B'	Dark green liquid with orange liquid organic layer	Dark green liquid with orange liquid organic layer	Dark green liquid with some brown gas and orange layer
6	3 M V(IV) 1.5 M Br <sub>2</sub> 0.75 M 'B'	Dark green liquid with orange layer	Dark green liquid with orange layer	Dark green liquid with orange layer

currently being conducted at lower temperatures and the complexed solutions are also being evaluated in charge–discharge cycling in small V/Br test cells.

#### 4. CONCLUSIONS

Of battery systems currently being commercialized around the world, the UNSW vanadium redox battery offers many advantages that make it suitable for a wide range of applications. The G1 VRF has already been successfully demonstrated in medium to large-scale field trials around the world for a range of stationary applications and new low-cost materials are now being used to achieve the necessary cost structure for full-scale commercialization.

Application of the G1 VRF battery in mobile systems has however been limited because of the low energy density of the vanadium sulphate electrolyte (20–35 Wh kg<sup>-1</sup>).

Significant improvements in energy density have been demonstrated with the new vanadium bromide redox fuel cell. A 3 M vanadium bromide electrolyte has already been verified and the use of bromine complexing agents has been shown to prevent the formation of potentially hazardous bromine vapour during operation of the V/Br cell. Further studies are currently underway to optimize and fully evaluate a complexed 3 M V electrolyte that will provide almost twice the energy density compared with the original all-vanadium redox flow cell, thereby providing a smaller system footprint in stationary applications, while also extending potential use in mobile systems such as electric buses and vans.

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