The vanadium redox flow battery in its present form was developed by Skyllas-Kazacos at the University of New South Wales in the 1980’s.[1, 2] An improved, multiple-stage layout of a 10 kW, 60 kWh vanadium redox flow battery is presented, with considerably reduced self-discharge. The system is compared and contrasted with one utilising a conventional layout.

Flow batteries are unique among rechargeable batteries in being able to effectively decouple the amount of energy stored with the maximum power output: tank size determines the energy, total electrode area the power. The vanadium redox flow battery has emerged as one of the most favourable types of flow batteries for a number of reasons, including the lack of cross-contamination that troubled many earlier systems such as the Fe-Cr redox battery.[3]

Typically in a flow battery reactor the electrolyte flows are divided by an internal manifold formed from the stacked arrangement of flow frames, such that each half-cell chamber is supplied with positive or negative electrolyte, as appropriate. The half-cells are physically separated by bipolar plates and ion-exchange membranes from adjacent half-cells. The membranes that divide a given cell allow transport of one ionic species (typically H⁺). However, they cannot completely hinder movement of the electroactive species. In the case of redox batteries with dissimilar electroactive species, such as the Fe-Cr system, this leads to a gradual mixing of the electrolytes, with consequent decrease in performance. Because the vanadium redox flow battery employs the same element in both electrolytes, albeit in different oxidation states, there is no cumulative loss in performance, just an effective reversible self-discharge current.

The simplest layout of a redox flow battery would be as shown in Fig. 1 with all of the cells contained within a single reactor.

To achieve this arrangement the individual cells may have a rather large area, which require high development costs, or there may be many small cells in series, leading to a high terminal voltage. Because all of the electrodes are at different potentials in common electrolytes shunt or bypass currents occur among them. This may be modelled by using a simple resistor network as an equivalent circuit.[4] The resistances were calculated by assuming the fluid lines to be completely filled with electrolyte and taking a linear approximation to the internal cell resistance, which was significantly smaller than that in the fluid lines, from experimental measurements. The parameters were appropriate for the cells and stacks used in the test system, operating at 25°C with 1.5 V potential difference per cell, i.e. the battery operating voltage was 60 V. The shunt currents through the cell string were calculated iteratively by solving Kirchhoff’s and Ohm’s laws with a microcomputer.

The results are shown below (Figs. 2 and 3) for 40 cells arranged as an undivided and as two, series-connected, 20-cell stacks. It is apparent that the divided stacks have significantly lower shunt currents than the undivided stack. This is due to the external manifold and flexible hoses between the stacks having much greater resistances than the internal manifold formed by the flow frames. It may also be easily shown by using the model that higher terminal voltages lead to higher average shunt currents.
Figure 2 Calculated shunt currents through 40-cell redox flow stack of 2 kW rated power

Figure 3 Calculated shunt currents through two series-connected stacks of 20-cells each, using the same cell parameters as in Fig. 2

To reduce the terminal voltages and shunt currents it was decided to provide a 10 kW battery with 5 strings of 2 kW, each string consisting of two series-connected 1 kW stacks, Fig. 4.
Self-discharge that occurs in the vanadium redox flow batteries is from both shunt-current losses and cross-over of vanadium species through the membrane: electrolyte stored in the tanks undergoes no appreciable self-discharge. The pumps also use power from the battery and may be considered as another source of self-discharge. It was found previously that the energy efficiency (full cycle) of the conventional vanadium redox flow battery was rather low, due to these losses, when the average power was low. [5]

Taking these considerations into account the layout of a 10 kW vanadium redox flow battery was modified in an attempt to reduce the self-discharge currents. The 5 strings were divided into 3 separate fluid circuits, Fig. 5. The first fluid circuit, containing a single string, was always actively pumped with electrolyte and electrically connected to the charger and load. The second and third fluid circuits contained 2 strings each and were only actively pumped and electrically connected when the bus voltage reached preset limits. Therefore, the operation of the battery was divided roughly into 0 – 2 kW, 2 – 6 kW and 6 – 10 kW stages, although other divisions could be relatively easily realised.

The 10 kW multi-stage test system is shown in Fig. 6. As can be seen the individual stacks were joined by flexible hoses to one of three pairs of rigid manifolds. The pairs of manifolds were in turn supplied by pairs of pumps, although all electrolyte originated from a single pair of tanks (one tank for negative electrolyte, one for positive).
When the circuits were in “standby”, i.e. not actively pumped and electrically connected, the self-discharge was limited to the small volume of electrolyte in the cells. There was also a saving in the pumping energy, because 3 pairs of small pumps were used in place of 1 pair of more powerful pumps. The multi-stage layout was compared with another system which used a single-stage layout, single stage (1), and with the same system operating under a single-stage regime, single stage (2). The batteries were cycled at constant power and the round-trip energy efficiency of the battery, including controller unit, sensors and pumps but not inverter or charger, calculated.

As can be seen from Fig. 7 the energy efficiencies of the batteries with as a single-stage layout were rather low at low operating powers. In contrast the multi-stage layout maintained high efficiencies from 6% to 120% of the rated operating power. It may also be noted that the single stage (1) system had lower energy efficiencies than the multi-stage at ≥60% of operating power, whereas they would be expected to be very similar, because at ≥60% of operating power all strings would typically be active. The difference is due to some optimisation in the cell design and pumping regime. However, as the single stage (2) efficiency was measured with the same battery as the multi-stage measurements the general conclusion that the multi-stage layout improved efficiency at lower average operating power holds true.
It may also be noted that the charge efficiency for the multi-stage system remained almost constant over the tested power range and that the decrease in energy efficiency at higher powers resulted almost entirely from the decrease in voltage efficiency, i.e. from resistive losses:

Figure 8 Voltage and charge (Coulombic) efficiencies of a multi-stage vanadium redox flow battery arranged against power
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