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Critical safety features of the vanadium redox flow battery

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HIGHLIGHTS

- Vanadium redox flow battery stacks were electrically short-circuited.
- Almost all of the heat flowed into the electrolyte.
- The stack behaved safely and remained undamaged under this type of abuse.
- Even membrane puncture did not cause excessive temperature rise.

GRAPHICAL ABSTRACT

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ABSTRACT

In this work the behaviour of the vanadium redox flow battery is examined under a variety of short-circuit conditions (e.g. with and without the pumps stopping as a result of the short). In contrast to other battery types, only a small proportion of the electroactive material, in a flow battery, is held between the electrodes at any given time. Therefore, together with the relatively low energy density of the vanadium electrolyte, the immediate release of energy, which occurs as a result of electrical shorting, is somewhat limited. The high heat capacity of the aqueous electrolyte is also beneficial in limiting the temperature rise. It will be seen that the flow battery is therefore considerably safer than other battery types, in this respect.

1. Introduction

The vanadium redox flow battery (VRFB) has gone from being a laboratory curiosity [1–3], to gaining significant commercial application over the last decades [4–7]. To date over a hundred systems have been installed worldwide, for stationary energy supply.

Redox flow batteries store energy chemically in positive and negative electrolytes. Most of each electrolyte volume is stored in a tank. Electricity is supplied by electrochemically discharging the electrolytes in cells, which are typically assembled into stacks. Fresh electrolyte is pumped (or rarely, fed by gravity [2,8,9]) from the tanks and through the stacks. Therefore, at any given time only a small fraction of the energy in the battery can be released as electricity. For a VRFB with 8 h of storage (i.e. can deliver the rated energy for 8 h at the rated power), the electrolyte in the stacks is of the order of 1% of the total volume. This is one of the reasons for suggesting that redox flow batteries are safe [10].

Battery safety is an important and topical issue. Many thousands of articles published on lithium-based batteries have considered some aspect of safety. In contrast very little has been reported on electrical safety of the VRFB [11], or other types of flow battery [12–14]. This is partly because they are intended for stationary applications, which are often unmanned.

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External short-circuits are very unlikely, and design measures are taken to hinder them, as far as possible. However, they can occur during service, maintenance and de-installation work, for example. Rather than attempting to estimate the maximum short-circuit current by extrapolation from discharge at different currents, which has been found to be inaccurate in some cases [15], it was decided to short a test stack through a very low impedance circuit.

Internal short-circuits are more common in hybrid flow batteries, where metallic dendrites can grow between the electrodes [16–18]. However, they can also result in this type of battery (for example, through degradation of the ion-exchange membranes [19]). An internal short-circuit was experimentally produced in a test stack and the physical consequences observed.

2. Experimental

To investigate the electrical safety of vanadium redox flow batteries (VRFBs), it was decided to conduct a series of short-circuit tests on standard, commercially-available, stacks. Stacks from the CellCube™ product series (Gildemeister energy storage GmbH) with 20 cells and 27 cells were used for the tests.

The stacks were initially used to charge vanadium electrolyte to 83% state-of-charge (SoC) on a purpose-built test-rig with 115 L of positive electrolyte and 115 L of negative electrolyte. This limit is the same as that commonly employed in commercial systems, to prevent overcharging of the stacks.

So called generation 1 electrolyte was used [20], i.e. a solution of 1.6 mol l^{-1} V with 4.2 mol l^{-1} total sulphate (as a mixture of sulphuric acid and vanadium sulphates).

The SoC was determined by use of a single cell at open-circuit, connected fluidically in parallel with the test stack [21].

After charging, the stack was immediately disconnected from the charging circuit and connected to a shorting test-circuit, as shown in Fig. 1. The resistance of the shunt resistor was 60 μΩ, the cable resistances were 620 μΩ, and the closed relay plus contact resistance of the cable shoes were measured at 230 μΩ. For comparison, a 20-cell stack has an internal resistance of ~60 mΩ, under normal cycling conditions. The current was determined by measuring the voltage across the shunt resistor, and the stack potential difference was measured directly from the terminals. The data was recorded every second. Shorting was initiated by remote activation of the high-current relay, roughly 60 s after commencing data recording. At this point the SoC of the electrolyte in the stack was still ~83%.

For the different tests the pumps were either switched off, in which case a residual total electrolyte volume of ca. 365 ml $cell^{-1}$ remained in the stack, or the electrolyte was circulated between the stack and the tanks using magnetically-coupled, centrifugal pumps. In the cases, described in the results section, where electrolyte did not flow, the pumps were switched off within 300 s prior to commencing the short-circuit test.

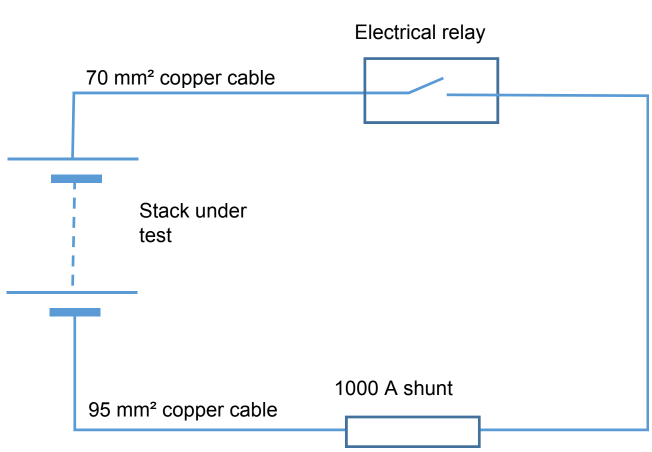

Fig. 1. Schematic illustration of the electrical shorting test-circuit.

Temperature measurements were made directly by connecting Pt1000 sensors to the outer (plastic) frame of the stack and the positive and negative connectors. Additionally a thermal camera (Fluke) was used to examine the temperature distribution over the whole system.

The test stacks had previously been extensively cycled (for 100 days, in the case of the 20-cell stack), but were considered to be otherwise representative of typical stacks.

Stack cycling, to determine the cycle efficiencies, was performed at a constant current of 40 A, between the SoC limits of 10% and 83%. A fraction of the electrolyte was periodically transferred between the tanks to ensure that the fluid volumes remained roughly constant.

3. Results

3.1. Shorting with fuse

It is general practice to place fuses in the electrical circuit, between the stacks and other electrical components (e.g. bus bars or power electronics). Therefore, if a short were to occur beyond the fuse a high current would flow through the stack for only a short time until the fuse breaks the circuit. To simulate short-circuit with fuse blow: a stack, without electrolyte flow, was shorted for 8 s (much longer than would be expected in practice).

The resulting current and potential difference across the stack terminals are shown in Fig. 2.

The current peaked at 730 A, and stack voltage dropped to ~0.6 V, corresponding to an internal resistance of 42 mΩ. This is lower than the observed resistance during cycling (ca. 60 mΩ). Therefore, although the resistance obtained by cycling can be used to give a first approximation to the short-circuit current, actual shorting is required to make a more accurate determination. The use of impedance under open circuit voltage (OCV) or low current conditions, will be similarly misleading [22]. The test-circuit shown in Fig. 1 is suitable for this type of measurement, assuming other relevant safety precautions are observed.

The stack was returned to an open-circuit condition after 8 s, upon which the voltage recovered to 28.36 V. Assuming an internal electrolyte temperature of 40 °C this would correspond to a final electrolyte SoC of 63%. Therefore, the electrolyte had decreased by 20% in SoC, through the passage of 1.50 Ah. This would indicate an average of 350 ml $cell^{-1}$ of accessible electrolyte in the stacks (i.e. not in the internal manifolds). This is very close to the expected volume of 365 ml $cell^{-1}$, indicating that the stacks had not drained significantly, during deactivation of the pumps.

The temperature rise of the terminals (T contact+ and T contact-) and distance holders (T frames) was measured at ≤0.5 K, Fig. 2. Thermal images showed no significant temperature rise in the cables, stack or contacts. The stack cycled normally after shorting.

3.2. Full-short, no pumping

On removal of a stack from a system, for example during decommissioning, it is likely that, at least some of the electrolyte remains in the cells. In the worst case all of the electrolyte would remain in the stack, in a highly-charged state. If proper care is not taken during this operation, electrical short-circuiting could occur. To simulate this event, the test stack was shorted until the current