



Pulsating electrolyte flow in a full vanadium redox battery



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HIGHLIGHTS

- Intermittent electrolyte flow strategy has been applied to vanadium flow battery.
- Different no-flow intervals have been tested.
- Reduction of >50% of pumping energy while maintaining high EE of 80.5%.
- Slight decrease of 3.4% in EE is due to increased concentration polarization.

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ABSTRACT

Proper management of electrolyte flow in a vanadium redox battery (VRB) is crucial to achieve high overall system efficiency. On one hand, constant flow reduces concentration polarization and by extension, energy efficiency; on the other hand, it results in higher auxiliary pumping costs, which can consume around 10% of the discharge power. This work seeks to reduce the pumping cost by adopting a novel pulsing electrolyte flow strategy while retaining high energy efficiency. The results indicate that adopting a short flow period, followed by a long flow termination period, results in high energy efficiencies of 80.5% with a pumping cost reduction of over 50%.

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1. Introduction

Vanadium redox batteries (VRBs) are a potential solution to the ever increasing demand for large scale energy storage devices in the twenty-first century. One of the major advantages VRBs offer over other flow batteries with different chemistries is their resistance to electrolyte cross-contamination, giving them a theoretically infinite lifespan. First pioneered by Skyllas-Kazacos at the University of New South Wales [1–3], research has mainly focused on electrode [4–9], electrolyte [10–12] and membrane treatment [13,14] in order to achieve high energy efficiencies.

In comparison, much fewer work has been performed in the area of increasing *system level* efficiency, particularly in addressing the primary source of auxiliary power consumption – the pumps used to drive electrolyte through the VRB. For a near-to

optimal design, these pumping energies have been shown to lower efficiencies by close to 10% [15]; this could potentially be higher if shunt current reducing designs are adopted via extending the channel lengths. In addition, pumps have been estimated to cost between 5 to 14% of the entire capital cost of a VRB system [16]. It is therefore of interest, both from an efficiency and cost point of view, to attempt to reduce the pumping power or frequency of a VRB. To this end, Ma et al. [17] introduced a strategy in which the flow rate is kept low for the bulk of the charging process and increased 3.5 times towards the end of charging. This allowed them to reduce concentration polarization, which primarily manifests itself towards the end of charge, whilst keeping the system efficiency at 66.5%. Tang et al. [18] took this concept one step further and demonstrate via simulations the feasibility of applying a fully variable flow rate by maintaining a pre-determined stoichiometric number throughout the charge–discharge cycle. One common point between these two studies, however, is that the pumps need to be in constant

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operation, which could potentially lead to higher wear and by extension, maintenance cost.

This work seeks to demonstrate the use of pulsating electrolyte flow with various resting intervals in order to reduce the pumping energy required. It also aims to elucidate the impact of concentration polarization during no-electrolyte flow regimes in a VRB in contrast to continuous flow systems. The unoptimized results indicate that significant reductions of more than 50% in pumping energy can be achieved whilst incurring an energy efficiency loss of only 3.4%, implying that adopting such a flow strategy could improve the system level efficiency of a VRB.

2. Experimental procedures

A single cell VRB was fabricated in-house to study the effects of pulsating electrolyte flow on its performance. The cell comprised stainless steel end plates, porous carbon felts to act as electrodes, graphite bipolar plates, gaskets and a proton exchange membrane. The carbon felt (SGL, Sigracell GFD 4.6 EA) was heat treated at 400 °C for 24 h to activate its surface and increase its hydrophilicity. The membrane (Nafion 115 from Ion Power) was soaked in boiling 3% H₂O₂, boiling 0.5 M sulfuric acid and boiling de-ionized water for 1 h each, in that order. In-between each step, it was further rinsed with de-ionized water.

The dimensions of each electrode after assembly were 5.4 cm (streamwise) by 3.7 cm (spanwise) by 3 mm (thickness), corresponding to an effective area of 20 cm², a compression ratio of approximately 30% and a final porosity of 89%. It was operated in co-flow mode at room temperature of 25 °C. A separate small monitoring cell was placed at the outlet of the single cell to monitor the open circuit potential. The monitoring cell was constructed using identical materials and had an effective area of 1 cm².

Two peristaltic pumps of the same type (Williamson Manufacturing Company Limited) circulated the electrolyte. Prior to operation, the flow rate was calibrated *in situ* by varying the voltage and measuring the time taken to cycle 20 ml of electrolyte. The calibration was repeated 5 times to ensure repeatability. The flow rate was 0.361 ± 0.002 ml s⁻¹ for both positive and negative electrolytes in all experiments. An in-house fabricated control board was used in tandem with a power source to operate the pumps in pulsation mode as well as to measure the total energy consumed.

The electrolyte was formulated by first dissolving the appropriate amount of vanadyl sulfate (Aion Scientific Pte Ltd) in 3 M sulfuric acid to give 1.5 M VO²⁺. 50 ml of the electrolyte was placed in the positive tank and 25 ml was placed in the negative tank. The electrolyte was then charged at a constant current (50 mA cm⁻²) and subsequently at constant voltage (1.65 V) to obtain yellow VO₂⁺ solution in the positive tank and violet V²⁺ solution in the negative tank. 25 ml of the VO₂⁺ was removed and the electrolyte fully discharged to yield 25 ml of 1.5 M VO²⁺ as the positive electrolyte and 1.5 M V³⁺ as the negative electrolyte. During all experiments, nitrogen was continuously pumped into both tanks to prevent unwanted oxidation of V²⁺.

A potentiostat/galvanostat (Metrohm, Autolab PGSTAT302N with FRA32M) charged and discharged the single cell at a constant current of 1 A (50 mA cm⁻²); it measured the potential difference across the single cell. The monitoring cell, along with a personal computer, kept track of the open circuit voltage. The open circuit voltage provided a measure of the state-of-charge (SOC) of the VRB and controlled when to switch from charging to discharging of the single cell or vice versa. While other SOC measurement methods have been reported in literature, for instance absorption spectroscopy [19], UV–vis and conductivity based measurements [20], using the open circuit potential was the easiest and required the least

amount of hardware. A schematic of the overall experimental setup is illustrated in Fig. 1.

3. Results and discussion

3.1. State-of-charge calibration

One charge–discharge cycle was first performed on the single cell under galvanstatic conditions of 50 mA cm⁻² for a voltage range of 0.8–2.0 V. Both the single cell potential as well as the open circuit potential were recorded simultaneously as shown in Fig. 2. The steep change in single cell potential towards the end of charge and discharge implied that the electrolyte was close to full and zero charge respectively. The open circuit potential was observed to be symmetrical about the time of full charge, implying that both electrolytes were balanced. The difference between the single cell potential and open circuit potential is due to polarization, namely from activation, concentration and internal resistance. A quick comparison of the single cell voltage and open circuit potential in Fig. 2 shows that the polarization is generally SOC independent, except towards the end of charge and discharge, where concentration polarization increases significantly due to increased mass transfer limitations resulting from low relevant electrolyte concentration.

Based on the results shown in Fig. 2, the open circuit potential at SOC_s was found by recognising the linear relationship between time and SOC. The open circuit potentials corresponding to a SOC value of 10% and 90% were determined to be 1.33 V and 1.53 V respectively. Subsequent experiments were carried out within this open circuit potential range. The use of open-circuit instead of single cell potential as a control was to ensure that the battery was always cycled between the same SOC_s, in order to allow for fair comparison to be made with regards to energy efficiencies.

3.2. Effect of pulsating flow on performance

The setup was first charged and discharged under constant electrolyte flow rate to obtain the baseline performance. It was subsequently run with pulsating electrolyte flow with the convention *t*_{on}:*t*_{off}, referring to electrolyte flowing for *t*_{on} seconds followed by complete flow termination for *t*_{off} seconds and repeating periodically. A total of 4 different periods were tested: 10:0 (continuous flow), 10:5, 10:10 and 10:20. Fig. 3 shows the difference between the 4 periods. The 10 s of electrolyte flow, at the stipulated flow rate of 0.361 ml s⁻¹, was able to refresh 68% of the existing electrolyte within the electrodes per cycle. The time-averaged stoichiometric number is defined as

$$\xi_{charge} = \frac{FQ(1 - SOC)c^0}{|I|} \left(\frac{t_{on}}{t_{on} + t_{off}} \right) \quad (1)$$

$$\xi_{discharge} = \frac{FQ(SOC)c^0}{|I|} \left(\frac{t_{on}}{t_{on} + t_{off}} \right) \quad (2)$$

where *F*, *Q*, *I*, and *c*⁰ refer to Faraday's constant, volumetric flow rate, applied current and initial V³⁺ concentration respectively. The operating conditions corresponded to a range of stoichiometric numbers (computed at 90% SOC during charge) from 1.7 to 5.2; the former refers to the 10:20 setup while the latter refers to the continuous flow setup. The stoichiometric numbers adopted compare well against commercial VRBs; for instance, Ma et al. [17] adopted a stoichiometric number of 2.9 (computed at 90% SOC

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