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# Measurement of local current density of all-vanadium redox flow batteries

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#### HIGHLIGHTS

• Local current density is measured by two specially designed single cells.

• Variations of local current density during charge/discharge process are presented.

• Effect of electrolyte flow rate on current density variation is shown.

• Lower limit of state of charge during discharge process is evaluated.

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#### ABSTRACT

This article presents a preliminary study of the measurement of local current density in all-vanadium redox flow batteries. Two batteries are designed and manufactured in this study, and the experimental results are compared. In the first cell, the current collector is divided into 25 segments, and the flow field plate is not segmented, whereas in the other cell, the flow field plate is segmented. The effects of the electrolyte flow rate on the battery efficiencies and the local current density variation are investigated. The experimental results show that the current density near the outlet significantly decreases when the discharge capacity approaches zero. In addition, the battery has a larger discharge depth at a higher electrolyte flow rate.

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#### 1. Introduction

All-vanadium redox flow batteries (VRFBs) have garnered substantial attention over the past few years because of renewable energy storage requirements. A VRFB discharges and stores electricity through the redox reaction between vanadium ion oxidation states. In a VRFB system,  $V^{2+}/V^{3+}$  and  $V^{4+}/V^{5+}$  redox couples serve as the negative and positive electrolytes, respectively [1,2]. During discharge,  $V^{2+}$  is oxidized to  $V^{3+}$ , while  $V^{5+}$  is reduced to  $V^{4+}$ . In the charging process, these reactions proceed in the opposite direction. At the positive electrode:

At the positive electrode:

$$VO_2^+ + 2H^+ + e^- \xrightarrow[Charge]{\text{Discharge}} VO^{2+} + H_2O.$$
 (1)

http://dx.doi.org/10.1016/j.jpowsour.2014.06.081 0378-7753/© 2014 Elsevier B.V. All rights reserved. At the negative electrode:

### $V^{2+} \xrightarrow{\text{Discharge}}_{\text{Charge}} V^{3+} + e^{-}.$ (2)

Both the negative and positive electrolytes are stored in reservoirs outside the VRFB cell and are pumped into the cell stack during electrochemical reactions. Because of this, the energy capacity can be increased by simply adding more electrolytes to the reservoirs, and the output power is determined by the cell number and active area of the electrodes. Because the energy capacity is determined by the amount of electrolyte stored in the reservoirs and because the power output is determined by the cell stack, the power and energy of a VRFB system can be individually designed. Moreover, the positive and negative electrolytes are separately stored, resulting in low self-discharging. Because of these advantages over other energy storage systems, VRFB systems are considered potential candidates for large-scale energy storage and





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Fig. 1. A schematic of the experimental setup.

have been coupled to intermittent renewable power sources, such as solar or wind power systems [3–6]. In the coupled system, VRFB systems perform load leveling and peak shaving.

The major challenges for the commercialization of VRFBs are the key materials and system optimization, which significantly influence the efficiency of a VRFB system. Several studies have investigated the key materials, including electrolyte additives [7], sulfate—chloride mixed electrolytes [8], carbon paper electrode coated with supported tungsten trioxide [9], and modified separators [10–17], but few have focused on the system efficiency [18–20].

Ma et al. [18] experimentally studied the effect of the electrolyte flow rate on the performance of VRFBs operating at different current densities and proposed an optimal strategy for the electrolyte flow rate. They suggested that at each operating current density, the electrolytes should be supplied with either low or high flow rates, depending on the cell voltage. Ma's



Fig. 3. Charge-discharge curves of cell A at 60 mA cm<sup>-2</sup>.

experimental results also showed that the capacity and efficiency increased with increasing electrolyte flow rate. Benjamin et al. [19] compared the battery efficiencies determined using cutoff voltages and SOC limits. Tang et al. [20] modeled the concentration overpotential as a function of the electrolyte flow rate to investigate the effect of the electrolyte flow rate on battery efficiency. They suggested an optimized variable flow rate with a flow factor of 7.5, which resulted in higher system efficiencies over constant flow rates. When the electrolyte flow rate increased because of a low reactant concentration, the concentration overpotential was reduced. Although the effect of the electrolyte flow rate on cell performance has been studied, its effect on local current density has not been reported as far as we know.

In this study, two VRFB cells are designed for the measurement of local current density. The major difference in the design is the method of dividing the active area. The experimental results of the two designs are compared and discussed. The effect of the electrolyte flow rate on the current density distribution is also studied.

#### 2. Experimental

The experimental setup, which consists of the VRFB single cell, electrolyte recirculation system, and the measurement system, is illustrated as Fig. 1.



Fig. 2. Schematics and photos of the two cell designs used in this study. (a) Cell A: gold-plated current collector divided into 25 segments. (b) Cell B: graphite flow field plate divided into 25 segments.

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