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Study of flow behavior in all-vanadium redox flow battery using spatially resolved voltage distribution

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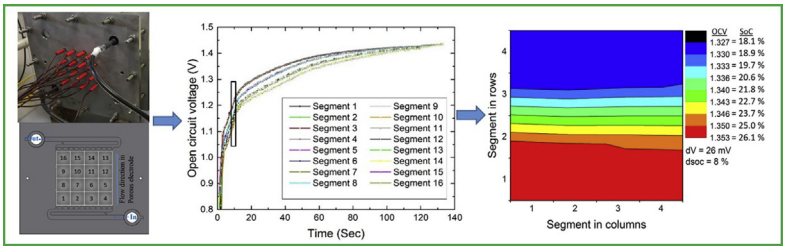
HIGHLIGHTS

- Positive half-cell of a 100 cm^2 conventional VRFB was segmented.
- Segmentation of porous felt electrode for the first time in VRFB.
- Segmented felt improved resolution.
- Flow patterns reflected in OCV contour maps.

GRAPHICAL ABSTRACT



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ABSTRACT

Uniform flow distribution through the porous electrodes in a flow battery cell is very important for reducing Ohmic and mass transport polarization. A segmented cell approach can be used to obtain in-situ information on flow behaviour, through the local voltage or current mapping. Lateral flow of current within the thick felts in the flow battery can hamper the interpretation of the data. In this study, a new method of segmenting a conventional flow cell is introduced, which for the first time, splits up both the porous felt as well as the current collector. This dual segmentation results in higher resolution and distinct separation of voltages between flow inlet to outlet. To study the flow behavior for an undivided felt, monitoring the OCV is found to be a reliable method, instead of voltage or current mapping during charging and discharging. Our approach to segmentation is simple and applicable to any size of the cell.

1. Introduction

Redox flow batteries (RFB) offer the unique advantage of allowing independent scaling of power output (in kW) and energy storage capacity (in kWh). Out of various chemistries available in RFBs, the all vanadium redox flow battery (VRFB) is the most widely used chemistry in commercial systems. The VRFB constitutes a safe, durable and commercially-available technology, which benefits largely from the fact that both half-cell electrolytes contain vanadium species at different oxidation states dissolved in sulfuric acid [1,2].

In a conventional VRFB, thick (3–6 mm) and highly porous

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(>90%) carbon fiber-based electrodes are used in order to provide high specific surface area for the redox reactions. Prior to assembly, the electrodes are commonly subject to surface treatment in order to improve wettability and reactivity. Flat sheets of carbon or graphite without flow fields are used as a bipolar plate (BP). In this configuration the electrolyte is forced to flow through the cross section of the porous felt electrode. Ideally, the electrolyte should distribute uniformly through the electrode. However, flow non-uniformity may occur due to various reasons such as improper design of flow frame, non-uniform or excessive compression of the felt electrode, uneven wettability of the bulk electrode or non-uniform thickness of the electrode material. A non-uniform flow distribution can result in non-uniform current distribution, with the possibility of locally overcharging the electrolyte, which, in turn, causes gas evolution and degradation of the BPs [3].

A non-uniform flow distribution also increases Ohmic and mass transport polarization, which eventually reduces the battery performance. Therefore, numerous studies in VRFBs have been focused on improving the flow distribution through the porous electrode using different approaches, such as operation at above the stoichiometric flow rate [4–6], use of flow channels in the BPs [7–10] and in porous electrode [3,9], use of optimal electrode compression [11,12], increasing the flow velocity through the felt [5] and use of thinner electrodes [13–15].

The optimal flow rate in a flow cell or stack can be determined simply by studying polarization curves and charging/discharging cycle behavior at various current densities. However, confirming a uniform flow distribution inside the porous electrode during the operation of the cell remains difficult. Some ex-situ techniques such as dye, pH or salt tracing [16], thermal dispersion [17], imaging techniques [18], etc. Have been used in various areas of engineering for the study of flow distribution. Since only small temperature gradients are formed during operation and due to the strong optical absorbance of the electrodes, thermal dispersion and imaging techniques or dye tracing are not suitable. Salt or pH tracing, however, are unable to provide the real time localized information of the cell during operation.

Spatially resolved local current and voltage mapping in a segmented cell is a unique and strong tool to investigate the in-situ behavior of the cell. This approach is well established in PEM fuel cell research [19–24]. By contrast, segmented cell studies of flow batteries are scarce [25–28]. Hsieh et al. [25] divided the positive half-cell of a 100 cm^2 size conventional flow cell into 25 segments and used a shunt resistor network to measure the current and voltage of each segment. Two designs were tested, one with a segmented copper collector, without segmenting the graphite flow field plate (5 mm thick) and secondly with the segmented graphite collector (10 mm thick) plugged directly into the banana plug connector. Due to the variation in the contact resistance among segments, non-uniform compression of the electrode and use of a non-segmented thicker plate in their first design, lateral flow of current largely affected the current distribution. In their second design, the cell suffered from the higher contact resistance resulting in lower voltage efficiency and discharge capacity. Clement et al. [26] segmented a 9 cm^2 VRFB single cell with a serpentine flow channel architecture using a Printed Circuit Board (PCB) technique, similar to a fuel cell design. The flow field plate was divided into 36 segments. Their study was focused in understanding the effect of electrode (carbon paper) properties and flow rate on local current distribution. The results showed that current distribution changed with varying thickness of the carbon paper and depended on flow rate, electrode wettability, and electrode porosity. Though their findings suggest that the local current distribution reflects the combination of local electrolyte velocity and electrolyte concentration, a more detailed study of flow behavior in a conventional design with a reasonable size of flow cell is necessary. The convection of reactants through the porous carbon paper in fuel cell-type cells is in the through-plane direction to the electrode, whereas, the electrolyte convection through the porous felt in a conventional VRFB is in-plane. Gandomi et al. [27] studied the through-plane potential distribution in multi-layer electrodes, by using the dynamic hydrogen electrode (DHE) concept in the VRFB. In a fuel cell-type cell architecture (zero gap), three layers of carbon paper electrodes were stacked and platinum wire electrodes were inserted between each layer of carbon paper as reference electrodes. The cell used two membranes with two platinum wires inserted as working and counter electrodes. Their experimental and simulation results showed that the mass transport polarization in through-plane concentrated towards the flow field plate. Becker and co-workers [28] introduced six potential probes into the graphite porous electrode of active area 100 cm^2 in order to measure the effective resistance of the graphite electrode at different cell compression and flow rates. Their results showed the dependency of the effective resistance of the felt on the flow rate towards electrolyte inlet at low compression.

As mentioned above, the segmented cell approach has not yet been used widely in a redox flow battery. In addition, none of the studies directly focused on understanding the flow behavior as a function of different operating conditions. Due to the use of thick and highly compressible porous electrodes in a larger area flow cell, the risk of uneven compression as well as unequal contact resistances exist at the electrode-BP interface. In addition, decrease in resistance of the electrode at the flow inlet side was observed with increasing flow rate, mainly at low felt compression [28], which could also result in non-uniform distribution of resistance on a local level. The unequal contact resistances among the segments may cause the segmented cell to suffer from lateral flow of current from one segment to another, giving rise to a misinterpretation of the data gained from the local current-voltage mapping [25]. As a consequence, it becomes unclear whether local current or voltage distribution in a segmented cell can be used for studying flow distribution in a flow cell.

Motivated by the work of Hsieh et al. [25] and Clement et al. [26], we present a simple design of segmenting a conventional flow cell that can be easily scaled up to any size. In order to minimise the issue of lateral flow of current, we propose the use of local mapping of open circuit voltage (OCV) alternative to common charging or discharging voltage or current mapping as a parameter to study the flow behavior in a flow cell. In addition to segmenting the BP and copper collector (CC), the graphite felt electrode was also segmented in selected cases to compare the change in resolution of the local voltage distribution.

2. Experimental

2.1. Test cell and experimental setup

The BP and CC of a positive half-cell in a 100 cm^2 (10 cm × 10 cm) active area size VRFB single cell were divided into sixteen segments. An exploded view of half-cell components at the segmented side are shown in Fig. 1.

The segmentation was done by modifying the insulator plate of the conventional flow cell design. Sixteen cavities were milled in the insulator plate to accommodate the segmented CC and segmented BPs. Holes were drilled in the end plate to allow banana plugs to insert into the CCs. The other components were similar to those of a single cell. The flow frame was made of PVC material milled with integrated flow guides. The back side of the flow frame consisted of a cavity for the BP to be attached for the non-segmented side. By the use of silicone gaskets, the cell was protected from internal and external leakage of electrolyte.