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Effect of flow field geometry on operating current density, capacity and performance of vanadium redox flow battery

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HIGHLIGHTS

- Graphite felts with/without flow field show high power density like carbon papers.
- Mass transport issues in VRFBs with various flow fields have been quantified.
- SFF offers better depth of discharge at low SOC.
- IFF performs better at low flows and currents and exhibits lowest pressure drop.
- CFF shows least mass transport resistance and has the highest pressure drop.

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ABSTRACT

Addition of flow fields to carbon paper electrodes in a vanadium redox flow battery (VRFB) can improve the peak power density through uniform distribution of electrolyte in the electrodes. However, it is unclear whether flow fields have a similar effect with graphite felt electrodes, as VRFBs with felt electrodes reported in literature show a large anomaly in obtained power density. In this work, we evaluate three flow fields; viz. serpentine, interdigitated and conventional (without flow pattern) type with felt electrodes and compare their performance with a serpentine flow field using carbon paper electrodes under identical experimental conditions. The conventional flow field provides highest energy efficiency (75%) followed by serpentine (64%) and interdigitated (55%) at 0.2 A cm^{-2} attributable to the deteriorating electrolyte distribution in the electrodes. Computation fluid dynamic simulations confirm the experimental finding of worsening electrolyte distribution (conventional < serpentine < interdigitated). A power density of 0.51 W cm^{-2} at 60 mL min^{-1} flow rate is obtained for serpentine and conventional flow fields with felt electrodes; comparable to the highest power density reported in literature for high performing zero-gap flow field architecture. This paper gives comprehensive insights on flow fields for VRFBs that can be extended to other flow batteries.

1. Introduction

Renewable energy sources such as wind and solar are intermittent and need large-scale electrochemical energy storage (EES) alternatives [1]. The potential of vanadium redox flow batteries (VRFBs) as a grid-scale energy storage solution is well documented [2–4]. The VRFB connected to the grid not only stores excess electricity but also helps with peak shaving, and grid-stabilization by providing energy during peak demand [5]. Moreover, thanks to its fast response to dynamic loads, VRFBs can also be used in hybrid distributed power generation systems along with fuel cells [6]. Intermittent energy production systems in combination with VRFBs can provide robust and sustainable power distribution. VRFBs possess distinct advantages over other flow battery chemistries for large-scale EES. VRFBs consist of positive electrolyte (VO^{2+}/VO_2^{+}) and negative electrolyte (V^{2+}/V^{3+}) dissolved in sulfuric acid or mixture of sulfuric acid – hydrochloric acid separated by an ion exchange membrane [7]. The redox couples in both the anolyte and catholyte are derived from vanadyl sulfate. Therefore, the cross-contamination, which is inevitable, does not result in the loss of electrolyte. Instead, spent and cross mixed electrolytes could be remixed and rebalanced for metal ion – acid concentration, which provides VRFBs a distinct edge over other flow battery technologies in terms of

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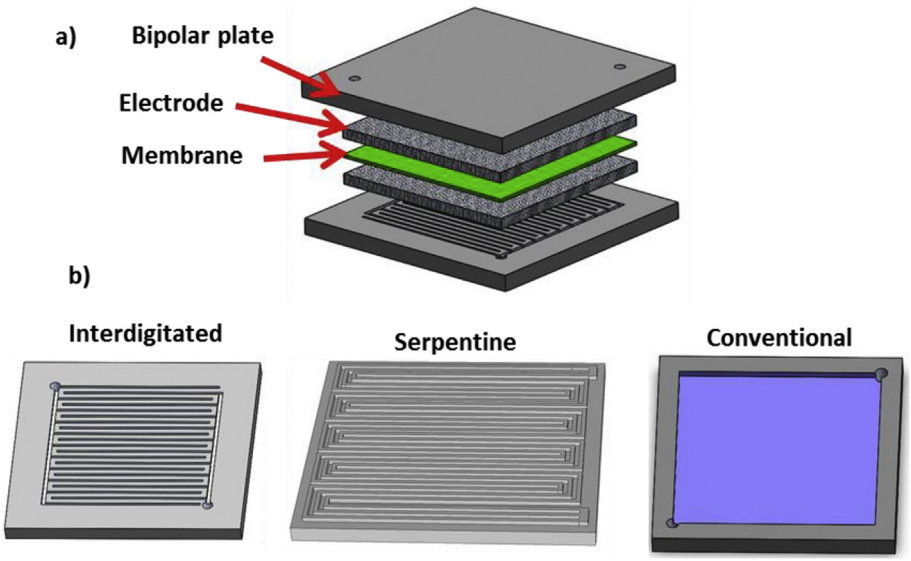

Fig. 1. a) Flow battery assembly and b) flow patterns: interdigitated, serpentine and conventional.

electrolyte costs [8].

The low energy density due to cross mixing and inherent solubility limit of vanadium sulfates in sulfuric acid, is a major hurdle for commercialization of VRFBs. Therefore, significant research has focused on the development of suitable membranes such as positively charged anion exchange, and porous membranes for minimal cross mixing [9–14]. Although the energy density of VRFB is still considerably less ($< 30\ \mathrm{Wh\ L^{-1}}$) than the lithium-ion batteries ($> 150\ \mathrm{Wh\ L^{-1}}$ [15]), increasing the volume of electrolytes of a VRFB can instantly increase the total capacity while increasing the number of single cells in a stack increases the power output. Therefore, a simple operation of sizing up the electrolyte tank and cell stack independently increases the energy and power output respectively, which is a considerable advantage of VRFB over secondary batteries such as Li-ion battery [16]. However, addition of each module consisting of membrane, electrodes, and bipolar plates further adds to the overall system costs [2]. Therefore, improvement in the power density of VRFB remains important to improve efficiency and reduce the tank size and stack size for any given peak demand. The higher power density could be realized by high output current at operating voltage [17].

Several previous reports state that the power density of VRFBs is $< 0.2\ \mathrm{W\,cm^{-2}}$ owing to the higher internal resistance and significant mass transport issues associated with the thicker graphite felt [18,19]. Introduction of flow fields and the use of thin and dense carbon paper electrodes in combination with flow fields have greatly improved the power density (up to $0.55\ \mathrm{W\,cm^{-2}}$) due to reduced internal resistance, better distribution of electrolyte and less parasitic pump losses [17,20]. However, the improvement in power density was insignificant when felt was used in conjunction with flow fields [18]. The graphite felt based VRFB showed improved performance when 1 mm thick felt was compressed by 80%, clearly demonstrating the dominant role of internal resistance on VRFB performance [21]. Recently, Davis and Tummino have also shown that felt electrodes after compression can have similar internal resistance and VRFB performance similar to that of carbon paper electrodes [22]. However, the performance reported in these studies varied from 0.2 to $1.4\ \mathrm{W\,cm^{-2}}$ even when the difference in internal resistance was small [17,20–22]. Theoretically, polarization curves should not be notably different in the activation and ohmic region when similar membranes and electrolyte concentrations are utilized. The only notable difference should be observed in the mass transport region due to the use of thick electrodes. However, a five-fold increase seen with carbon paper indicates that the polarization curves of traditional VRFBs with felt should be analyzed with more care. The polarization curves reported in the literature were obtained under different operating conditions, cell size and electrolyte conditions, which obscures their direct comparison. VRFBs are fundamentally transient systems like any other battery, therefore, polarization curves should be obtained with quick scans of potential or current. Fast scans minimize the depletion of State of Charge (SOC) locally in the cell compartment while providing the proper polarization curves.

In this study, we have investigated both graphite felt and carbon paper electrodes and resolve reported discrepancies in polarization performance between these two configurations. We report high power density VRFBs using felt electrodes similar to other publication [22] and provide alternative routes (other than compression) to improve power density of graphite felt electrode based VRFBs. We investigate VRFBs with serpentine, interdigitated, conventional, and zero gap configuration with serpentine flow field, for their polarization behavior and cycling performances. An improved method to record the polarization curves without depleting the SOC locally is used to compare the performances. The effects of flow fields, flow rate, SOC and cell geometries on polarization curves have been evaluated. Computational fluid dynamic (CFD) modeling of electrolyte flow field distribution in the channels and electrodes is also used in this work to examine the effects of mass transport on the performance of flow field geometries and pressure drop. This study for the first time resolves discrepancies reported in the literature on the performance of graphite felt and graphite paper electrode with and without the use of flow fields.

2. Methods

2.1. VRFB mass transport model

The computational domain consists of the bipolar plate with machined channels and the porous electrode graphite felt with an overall flow cell area of $5 \times 5\ \mathrm{cm^2}$. Three types of flow field configuration were used in this study: interdigitated, serpentine and conventional, (as shown in Fig. 1). The dimensions of the serpentine channels are: groove width 0.7874 mm, groove depth 1.016 mm, 30 grooves; interdigitated channels are: groove width 0.7874 mm, groove depth 1.016 mm, manifold width 1.173 mm, manifold depth 2.54 mm. The conventional flow field (CFF) does not have flow channels, instead the felt is placed in a 1.75 mm deep $5 \times 5\ \mathrm{cm^2}$ square trench with the inlet and outlet placed diagonally. For each simulation case, the inlet flow rate was kept at $40\ \mathrm{mL\,min^{-1}}$ to match with experimental flow rate. No slip boundary condition applied at the walls, and a constant-pressure boundary