



## Identification of performance limiting electrode using asymmetric cell configuration in vanadium redox flow batteries

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### H I G H L I G H T S

- ▶ Performance of a VRFB is investigated using asymmetric electrode configuration.
- ▶ Three different electrodes (i.e., raw, acid- and heat-treated) are investigated.
- ▶ Electrode functionalization is found to have different effects on (+) and (–) half-cells.
- ▶ Negative half-cell reactions are found to limit the overall performance of a VRFB.
- ▶ Poor performance of (–) half-cell is due to the undesired hydrogen evolution.

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### A B S T R A C T

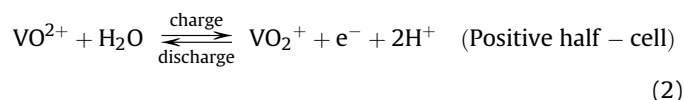
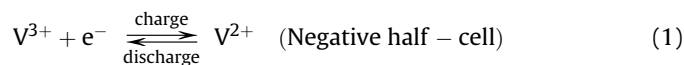
In this study, the performance of a vanadium redox flow battery (VRFB) is investigated using asymmetric electrode configurations with raw and functionalized (i.e., acid-treated and heat-treated) electrodes. The use of heat-treated electrodes in both half-cells is chosen as the baseline case for comparison, as this configuration shows the best performance. When the positive electrode in the baseline case is replaced with a raw or acid-treated electrode, the voltage efficiency is found to be comparable to that of the baseline case. However, in the case where the negative electrode in the baseline case is replaced with a raw or acid-treated electrode, a significantly lower efficiency is observed, suggesting that the negative half-cell reactions limit the performance of a VRFB. To further investigate this observation, an additional analysis is performed using cyclic voltammetry. The reaction kinetics data suggests that the poor performance of the negative half-cell is not due to the slow kinetics, but rather stems from the fact that the reduction reaction in the negative half-cell occurs at a potential that is very close to the onset of hydrogen evolution. The formation of hydrogen gas bubbles blocks the reaction sites and suppresses the favorable effects of functionalization in the negative half-cell.

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### 1. Introduction

The vanadium redox flow battery (VRFB) is an emerging energy storage technology, which offers unique advantages for use in large-scale energy storage. Unlike conventional batteries, the electrolytes are stored in external tanks and are circulated through an electrochemical cell. The key advantage of these systems is that power generation and energy storage are decoupled such that the energy storage capacity is determined by the amount of electrolyte in the storage tank and the electrolyte composition, whereas the power rating depends on the active surface area available for the electrochemical reactions in the VRFB cell [1,2].

A VRFB cell is composed of two inert porous electrodes which provide sites for the reactions, and an ion exchange membrane, which allows for ion transport between the half-cells to maintain electro-neutrality. The electrolytes in half cells are composed of differently oxidized vanadium species dissolved in sulfuric acid. The energy conversion process in half-cells occurs via following redox reactions:



where  $\text{VO}^{2+}$  and  $\text{VO}_2^{+}$  represent vanadium in the V(IV) and V(V) oxidation states, respectively.

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A key component that dictates the VRFB performance is the porous electrode which is responsible for enabling electrolyte transport, facilitating ion/charge transfer and providing reaction sites for electrochemical reactions. The internal structure and surface chemistry of the electrodes have direct implications on the transport related losses, electrolyte utilization, charge resistance and performance degradation. For instance, the available surface area in the electrode has a profound effect on the electrolyte utilization and system power output. In a recent study, Mench and his coworkers [3] have shown that the system performance can be significantly enhanced by increasing the total surface area of the electrodes. Similarly, the surface chemistry of the electrode governs the activation energy required to initiate the half-cell reactions. Depending upon the nature of the reactions, the surface chemistry of the electrodes may have an adverse effect on the reaction kinetics, which typically manifests itself as a decrease in output voltage and system efficiency.

Due to the highly oxidizing nature of V(V) ions, carbon and graphite are among the few materials that can be employed as electrodes in VRFBs [4,5]. In order to find the most compatible option, a variety of carbon based electrode materials (e.g., carbon nanotubes, oxidized graphite felt, and carbon-polymers) have been explored [6–9]. Among these, graphite felts, carbon cloths, and carbon fibers are shown to be the most promising candidates as they offer relatively high specific surface areas at a reasonable cost [10]. However, one major problem with these electrodes is that they possess very poor electrochemical activity, therefore showing poor kinetics for half-cell vanadium reactions. To address this issue, significant effort has been placed on improving the surface chemistry of these materials by introducing various functional groups [4,11–15]. Sun and Skyllas-Kazacos [11,12] have investigated the effects of thermal and acid treatments on the surface chemistry of carbon felt electrodes. Their studies indicate that surface treatment significantly increases the surface functional groups C–O and C=O at the electrode surface, which enhances the reaction rate in each half-cell. Similarly, Zhong et al. [13] and Yue et al. [4] have shown that introducing –OH and C=O groups considerably increases the electrochemical activity, reducing the activation overpotential of the electrodes. More recently, Wang and Wang [14] performed a study on Ir<sup>3+</sup> catalyzed electrodes. The Ir-modified electrode yielded very good electrochemical activity, particularly for the V(IV)/V(V) reaction. However, results for V(II)/V(III) reaction showed very poor activity, indicating that the use of same functionalization methods for both electrodes may not provide the desired performance.

Although the advantages of heat or acid treatment of the electrodes on the overall VRFB performance are repeatedly expressed in the literature, the exact contribution of these surface treatment methods on the positive and negative half-cell reactions remains unknown. Due to the different nature of the reduction and oxidation reactions, one of these redox reactions may limit the overall performance of the system. As a result, the same functionalization method might not be beneficial or appropriate for both half-cell electrodes. One potential approach to address this issue would be to identify the limiting half-cell reaction through a detailed analysis of the reaction kinetics in each half-cell. To date, studies reported in literature have been performed using symmetric configurations, where the same type of electrode (i.e., treated via the same functionalization method) was used for both positive and negative half-cells. As a result, it is very challenging to extract the key information from these studies with regards to which half-cell reaction is limiting the overall system performance. Such information would be very useful to understand the role of side reactions (e.g., hydrogen or oxygen evolution) on surface treatment and help to determine the optimum functionalization protocol for the VRFB electrodes.

In addition to the surface functionalization, understanding the reaction kinetics in each half-cell would have a direct impact on improving the resolutions of the VRFB models. Due to the paucity of experimental data, to date, the majority of the input parameters used in VRFB models are approximated or used as fitting parameters [16–24]. For instance, in the literature, very little information is available regarding reaction kinetic parameters, such as reaction rate constant ( $k$ ) and charge transfer coefficient ( $\alpha$ ), for the carbon felt electrodes. As a result, nearly every VRFB model uses the same reaction rate constant for both oxidation and reduction reactions. Moreover, most models assume that the charge transfer coefficient,  $\alpha$ , is equal to 0.5, though this has not been validated. Since the oxidation and reduction reactions in each half cell occur at different rates, it is very likely that the use of same reaction rate constants for both half-cell reactions might potentially yield inaccurate predictions of the activation overpotential and the cell potential.

This study is motivated by the need to better understand the half-cell reactions and their effects on the electrode functionalization. Our specific objective was to determine the limiting half-cell reaction by conducting performance analysis on differently functionalized VRFB electrodes using *asymmetric* electrode configurations (i.e., using different electrodes in positive and negative half-cells). Three different carbon felt electrode types, namely: raw, acid-treated and heat-treated electrodes were investigated via charge/discharge cycle testing. Cyclic voltammetry measurements were also conducted to determine the role of side reactions on the surface functionalization and quantify the key kinetic parameters, such as reaction rate constant and the charge transfer coefficient, for each electrode type, to provide a reliable set of input parameters for modeling efforts.

## 2. Method of approach

### 2.1. Electrochemical flow cell and electrolyte preparation

Charge/discharge cycling tests were conducted using a 10 cm<sup>2</sup> flow cell equipped with two composite graphite current collectors and two GFA5 (SGL Carbon Group, Germany) carbon felt electrodes, separated by a Nafion<sup>®</sup> 117 membrane. The GFA5 electrodes are made of a loose, random weave of graphitized carbon fibers with a thickness ranging from 2 to 5  $\mu\text{m}$  (see Fig. 1). Both raw and treated (i.e., heat-treated and acid-treated) GFA5 electrodes, which have 5 mm nominal thickness and 20% compression when the flow cell is assembled, were tested in this study. Heat treatment was performed by oxidizing the raw electrode at 400 °C in an air atmosphere for 6 h [13], while the acid treatment was performed by boiling the electrodes in 98% sulfuric acid for 6 h. Prior to testing, the Nafion<sup>®</sup> membrane was submerged in H<sub>2</sub>O<sub>2</sub> for 60 min at 80 °C, and then was placed in boiling deionized water for 60 min. After this step, the membrane was put into 0.5 M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 60 min, and then rinsed in boiling water for 60 min to remove any excess acid [25].

The electrolytes were prepared by filling each half-cell reservoir with a 60 ml solution of 1 M VOSO<sub>4</sub> (Sigma Aldrich, 97% purity) in 4 M H<sub>2</sub>SO<sub>4</sub>. Both reservoirs were de-aerated by bubbling nitrogen through the solution for 1 h. The electrolyte solutions were charged potentiostatically at 1.7 V to produce V<sup>3+</sup> and VO<sub>2</sub><sup>+</sup> for the negative and the positive half-cell reactions, respectively [26]. The positive half-cell solution was then replaced with 60 ml of the initial 1 M VOSO<sub>4</sub> solution to achieve an electrolyte solution that consists of 1 M V<sup>3+</sup> in 3.5 M H<sub>2</sub>SO<sub>4</sub> in the negative half-cell and 1 M VO<sub>2</sub><sup>+</sup> in 4 M H<sub>2</sub>SO<sub>4</sub> in the positive half-cell [27]. During charge/discharge testing, the electrolytes were stored under a continuous nitrogen blanket to prevent oxidation of the active species.

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