



Resistor Design for the Use of Dynamic Hydrogen Electrode in Vanadium Redox Flow Batteries



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ABSTRACT

Vanadium redox flow batteries (VRFBs) are attracting increasing amounts of attention for energy storage applications. However, their electrochemical performance capabilities have not been closely analyzed because proper reference electrodes remain elusive. In this work, we report the resistor design of a dynamic hydrogen electrode (DHE) for VRFBs which enables the in-situ monitoring of the positive and negative electrode potential. Due to the presence of multiple redox couples at the reference electrode inserted into the VRFB membrane, the adjustment of the current flowing through the DHE with the resistor is the key factor when attempting to maintain a stable and steady hydrogen reduction reaction at the DHE during repeated charge and discharge processes. With the insertion of the DHE into the membrane, the electrochemical properties of the positive and negative electrode/electrolyte can be individually analyzed. Thus, the DHE design provides an effective electrochemical analysis platform for VRFB research.

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1. Introduction

The vanadium redox flow battery (VRFB) is one of the most promising types of battery for use in energy storage systems owing to its ability to store large amounts of energy and its flexible modular design [1]. Furthermore, VRFBs have the advantages of a long cycle life, a short response time, and no cross-contamination [2–4]. Currently, VRFB technologies are evolving toward more energy-efficient and reliable systems through improved material development, better stack designs, and more suitable operation strategies [5].

In the VRFB research field, electrochemical performance measures such as the coulombic efficiency, voltage efficiency, and energy efficiency are measured by simply monitoring the cell voltage and current under various operation conditions. However, for an in-depth understanding, the collective and mixed contributions from the electrodes, electrolytes, and membrane should be separated and quantified through an electrochemical analysis, which requires individual measurements of the positive and negative potential. In this regard, a reliable and stable reference

electrode which allows for the in-situ monitoring of the electrode potentials is in high demand.

In spite of the importance of the reference electrode in an electrochemical analysis of VRFBs, there have been few studies of the design of a reference electrode. The main difficulty associated with the design of a reference electrode is the presence of various redox couples in the VRFB cell. The reference electrode potential can vary depending on the types and compositions of the electrochemical species, including V^{2+} , V^{3+} , VO^{2+} , VO_2^+ , and H^+ . One strategy with which to monitor the equilibrium electrode potential is to connect reference cells to the main cell [6]. When using this method, known as the ex-situ method, a small amount of the electrolyte effluent from the VRFB cell is supplied to one compartment of a reference cell, the other compartment of which is filled with a reference electrolyte of a known potential. By monitoring the voltage of the reference cell, the equilibrium potential of the electrolyte can be determined. The ex-situ method is useful for monitoring the state of charge (SOC) and the state of discharge (SOD); however, it does not provide any information about cell polarization.

Another possible strategy is the introduction of a reference electrode into a VRFB cell, which allows in-situ measurements of the positive and negative potentials of the VRFB cell. Ventosa et al. [7] conducted an in-situ operando study by inserting a reference

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electrode of silver wire, which exhibits the equilibrium potential of Ag/AgSO_4 , between two Nafion membranes. However, the contamination of the Ag electrode with various vanadium ions may not be completely prohibited, as the reference electrode is in contact with the vanadium electrolyte-swollen membrane. On the other hand, a dynamic hydrogen electrode (DHE), the most widely used type of reference electrode for fuel cells [8–13], can be employed as a reference electrode for VRFBs. By applying a small amount of current through the Pt electrode in a proton-containing medium, a reliable and stable hydrogen evolution reaction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) is induced at the Pt electrode. Although the potential under the hydrogen evolution reaction is lower than that of a standard hydrogen electrode (SHE), it approaches the SHE potential by minimizing the overpotential of the hydrogen evolution reaction. The use of a DHE for an electrochemical analysis of VRFBs was initially reported by Aaron et al. [14,15]. Their works successfully demonstrated that by inserting the DHE between two membranes, the positive and negative potentials can be individually monitored and the electrochemical impedance spectra of each electrode can be measured. However, these works did not describe the details of the DHE design in spite of the practical importance of doing so. In fact, the DHE electrode for VRFBs should be carefully designed because various vanadium ions with different oxidation states near the DHE can influence the potential of the DHE.

Herein, we report the design process of a DHE for the in-situ monitoring of the positive and negative potential of a VRFB and demonstrate, for the first time, that an adjustment of the resistance in the DHE is a key factor to attain a stable reference electrode potential close to the SHE for use in a VRFB. The DHE has been previously used for the analysis of positive and negative redox reaction [14], the potential distribution measurement [16,17] and electrochemical impedance analysis [18] in VRFBs. However, these works did not provide any information on the design process of DHE; the electrochemical reactions occurring at DHE were even not described, and it was not informed that which electrode from the two Pt electrodes constructing DHE should be used as a reference electrode. Furthermore, these works did not deal with the importance of the resistance in DHE, although it is critical in attaining a stable reference potential close to standard hydrogen electrode potential. The key contribution of our work, being different from the previous works, is to provide a logical understanding of DHE design for VRFBs. The paper clearly describes the electrochemical reactions of DHE employed in VRFB, and informs the way to induce a stable hydrogen evolution reaction at Pt electrode in the presence of various vanadium ions, which has not been described so far. Furthermore, we verify the efficacy of the DHE with various electrochemical methods, including the galvanostatic intermittent titration technique (GITT) and a self-discharge analysis. This work can provide a practical guide with which to construct a VRFB cell with a DHE for an in-depth electrochemical analysis of a VRFB.

2. Experimental

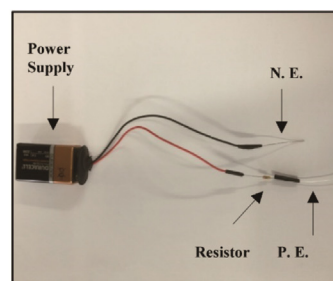
The VO^{2+} (V(IV)) electrolyte used here was prepared by dissolving 1.5 M $\text{VOSO}_4 \cdot n\text{H}_2\text{O}$ (99%, NewWell Co., $n=3.5$) in a 3 M sulfuric acid solution (95%, Aldrich). The VO_2^+ (V(V)) and V^{2+} (V(II)) electrolyte was electrochemically synthesized from the V(IV) electrolyte; 150 mL and 75 mL of the V(IV) electrolyte were added to a positive and negative tank, respectively, after which a cell 49 cm^2 in size was fully charged at a 61 mAcm^{-2} , forming the V(V) and V(II) electrolyte in the positive and negative compartment, respectively. After charging, half of the V(V) electrolyte (75 mL) was removed from the positive electrolyte tank to achieve a capacity balance between the positive and negative electrolytes.

The flow rate was 100 and 150 mL min^{-1} for the charge-discharge test and for the GITT respectively.

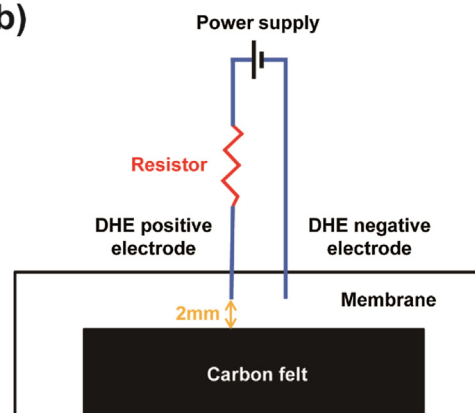
DHEs were fabricated by the following processes; one Pt wire (Aldrich, diameter of 0.5 mm) was connected to the negative terminal of a 9V battery (550 mAh) and the series of the other Pt wire and a resistance was to the positive terminal of the battery as illustrated in Fig. 1(a). The resistance was varied as 1.5, 15 and $155\text{ M}\Omega$. The Pt electrodes are positioned as such that the Pt electrode tips are 2 mm apart from the edge of the electrodes to avoid any interference by electric field generated between the two electrodes. The more detailed information on the configuration of DHE is given in the Supplementary Information.

A VRFB 49 cm^2 in size ($7\text{ cm} \times 7\text{ cm}$, Standard Energy Co.) was constructed by applying pressure of 0.5 MPa to a stack consisting of the positive end plate, positive electrode, membrane, negative electrode, and negative end plate. The carbon felt (NF-1311, Jihua Hi-Tech Co., Ltd, China) was treated at 400°C for 3 h in air condition. The two sheets of copper plate were used as a current collector. A Nafion membrane with a DHE inserted into it was fabricated by assembling two sheets of NRE 212 and the DHE, as shown in Fig. 1 (b), at room temperature. In order to avoid any

(a) Dynamic Hydrogen Electrode (DHE)



(b)



(c)

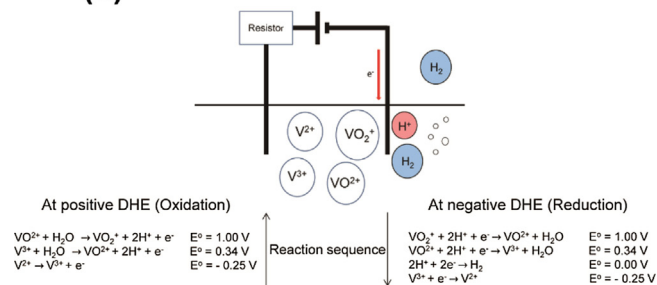


Fig. 1. Photo of (a) the DHE and (b) the DHE-inserted membrane; (c) scheme of the possible electrochemical reactions at the positive and negative electrode of the DHE.

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