

# In-situ investigation of hydrogen evolution behavior in vanadium redox flow batteries



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## HIGHLIGHTS

- An in-situ method to investigate hydrogen evolution in VRFBs is developed.
- The rate of hydrogen evolution during battery operation is quantified.
- The gas evolution behaviors in the charge process of VRFBs are observed.

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## ABSTRACT

In this work, we conceived and fabricated a three-electrode electrochemical cell and transparent vanadium redox flow battery to in-situ investigate the hydrogen evolution reaction during battery operation. Experimental results show that operating temperature has a strong influence on the HER rate. In particular, compared with  $V^{3+}$  reduction reaction, HER is more sensitive to temperature variation. It is also found that, contrary to the conventional wisdom that side reactions occur at the late stage of the charge process,  $H_2$  evolves at a relatively low SOC. About 0.26 and 1.94 mL  $H_2$  were collected at an early (SOC lower than 20%) and end of the charge process, respectively, suggesting that attention to the hydrogen formation at the negative electrode in the early charge process should also be paid to during long-term battery operations. Moreover, the produced hydrogen gas at the negative side prefers to form macroscopically observable bubbles onto the electrode surface, covering the active sites for vanadium redox reactions, while oxygen evolution (including  $CO_2$  production) at the positive side corrodes electrode surface and introduces certain oxygen-containing functional groups.

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## 1. Introduction

With the increasing concerns of environmental issue and ecological sustainability over the consumption of fossil fuels, renewable energy resources such as solar and wind have been attracted more and more attentions [1–3]. However, one major challenge limiting their practical use is the substantially fluctuated and intermittent nature [4]. Consequently, the development of economical and efficient energy-storage systems for load leveling, peak shaving, and uninterruptible power supplies becomes critically important at the current stage [5]. The vanadium redox flow batteries (VRFBs), which combine the advantages of independent power and capacity, significant alleviation of cross-contamination effect by employing the same vanadium element electrolytes, have been regarded as one of the most promising candidates for large-scale energy storage applications [6–9].

Since VRFB was initially proposed by Skvllas-Kazacos group [10], tremendous efforts including the development of electrolytes [11–13], membranes and electrodes [14–18], have been made toward improving the battery performance in the past few decades, such as energy density, power density and capacity retention of the system. However, capacity decay issue induced by vanadium ion and water across the membrane, and the tendency to develop asymmetrical valence of vanadium ion in electrolytes due to side reactions are still two critical technical barriers during battery operation [19]. As the potential of the negative electrode is below the dynamic hydrogen reference electrode, the lower potential thermodynamically allows for simultaneous hydrogen evolution reaction (HER) and  $V^{3+}$  reduction reaction on the negative electrode of the battery [20,21]. HER, as a parasitic side reaction during operation, not only consumes a portion of the charge current and covers some effective surface areas for redox reactions, lowering coulombic efficiency and energy efficiency of the VRFB system, but also results in an increase in the hydrogen concentration in the negative reservoir and the workshop, leading to a potential

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safety hazard [22]. Thus, the behavior of HER during VRFB operation remains to be investigated. Previously, Prof. Mench's group reported a series of work about the rate determining step in VRFBs via a dynamic hydrogen electrode [20,21,23] and found that the negative  $V^{3+}/V^{2+}$  couple contributed a larger portion of the total cell overpotential. Agar et al. further indicated that the formation of hydrogen gas bubbles blocked the reaction sites and suppressed the favorable effects of functionalization in the negative half-cell [24]. However, the above-mentioned work mainly focused on electrochemical kinetic study of vanadium redox reactions rather than side reactions during VRFB operation. Until now, there exist only a few works that deal with the issue associated with side reactions (e.g. hydrogen/oxygen evolution) during battery operation. In 2014, Sun et al. [19] demonstrated a quantitative method to determine the HER rate occurring at the negative carbon paper electrode. Recently, Schweiss studied different carbon fiber electrode with respect to the electrochemical kinetics for the HER [25]. They compared the HER rates by analyzing the effects of material crystallinity and functional groups. However, most experiments in their work were generally conducted ex-situ and hence provided limited information during real battery operation. Besides, these papers focused on electrode material effects rather than HER behaviors.

To elucidate the hydrogen evolution behavior more clearly and accurately, in-situ investigation is highly desired at the current stage. In this work, we conceived a home-made three electrode electrochemical cell and transparent battery to investigate the gas evolution behaviors in VRFBs. Through the transparent battery, gas bubbles in the channel could be visualized and recorded during battery operation. Besides, in our home-made three electrode electrochemical cell, the face of the graphite electrode was turned up. The generated gas bubbles can easily detach the surface of electrode by buoyancy and can be collected in a burette. Thus, HER current and coulombic efficiency can be measured accurately. The research method is based on a combination of in-situ visualization and quantitative measurement during battery operation. Gas evolution behaviors were monitored and their influence on electrode morphology and composition was then analyzed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) techniques. The objective of this work is to provide an implication of reducing HER as a side reaction in the VRFB. The work is expected to benefit the comprehensive understanding of gas evolutions in VRFBs, which leads to a higher stability and energy efficiency of VRFBs in practice.

## 2. Experimental

### 2.1. Electrolyte preparation

Electrolytes were initially made by dissolving 1 M  $VOSO_4$  in 2 M  $H_2SO_4$ . These solutions were then put in an electrolytic cell with Nafion® 117 (Dupont, USA) as the membrane. During the charging step, the  $VO^{2+}$  converted to  $V^{3+}$  and  $VO_2^+$  in the negative and positive compartment of the electrolytic cell, respectively. Subsequently, 100 mL of electrolyte from the negative compartment was moved to the negative reservoir, while 100 mL of pristine 1 M  $VOSO_4$  in 2 M  $H_2SO_4$  was added to the positive reservoir as initial electrolyte.

### 2.2. Three-electrode gassing measurement system design

Potentiodynamic cathodic polarization curves were obtained on a CHI Instruments (CHI604) electrochemical workstation. Hydrogen evolution reaction rate on a graphite electrode was measured by a three electrode electrochemical cell. In this setup design, the face

of the working electrode was turned up. As a result, the produced gas bubbles can easily detach the surface of electrode by buoyancy and be collected in a burette. Thus, HER current and coulombic efficiency can be measured accurately by means of the method reported by Lam's work [26], as detailed in Fig. S1. The working electrode was made of graphite electrode ( $0.2826\text{ cm}^2$ ) and sealed with a PTFE cylindrical mould. A platinum mesh and a saturated calomel electrode (SCE) was employed as the counter and reference electrode, respectively.

### 2.3. Transparent battery visualization system design

A transparent VRFB was conceived and fabricated for the visualization study, as schematically depicted in Fig. 1. Commercially available graphite felt (SGL, GFA series) with an uncompressed thickness of 4 mm (active area of  $16\text{ cm}^2$ ) were used as positive and negative electrodes, and Nafion® 117 was employed as the membrane. To avoid acid corrosion, the bipolar plates were made of dense graphite with a thickness of 4 mm. Each bipolar plate consisted of two parts, including a single serpentine flow field (SSFF) equipped channel area and an extension ear area. The channel area acts as distributor for supplying the electrolytes to the porous electrode while the ear area serves as the current collector. The width of both ribs and channels is 2 mm and the length of the channel is 38 mm. For the visualization study, two transparent enclosures, each having a thickness of 30 mm, were made of poly methylmethacrylate. With SSFF channel equipped in the battery, the channel-blocking behavior would not occur at a given flow rate [27]. The produced gas bubbles will depart from the porous electrode to the channel with the flowing electrolyte and finally be collected at the reservoir.

### 2.4. Battery performance tests and characterizations

The battery operation conditions were controlled by an Arbin BT2000 battery testing system. Before battery test, nitrogen gas with high-purity was used to expel the residual air in the cell and electrolyte tanks. During the charge process, hydrogen concentration in the reservoir was measured by a gas chromatograph (GC) (SP-3400, Beifen Co.) equipped with thermal conductivity detectors (TCD) and a  $4\text{ m} \times 3\text{ mm}$  HayeSep column. Argon was acted

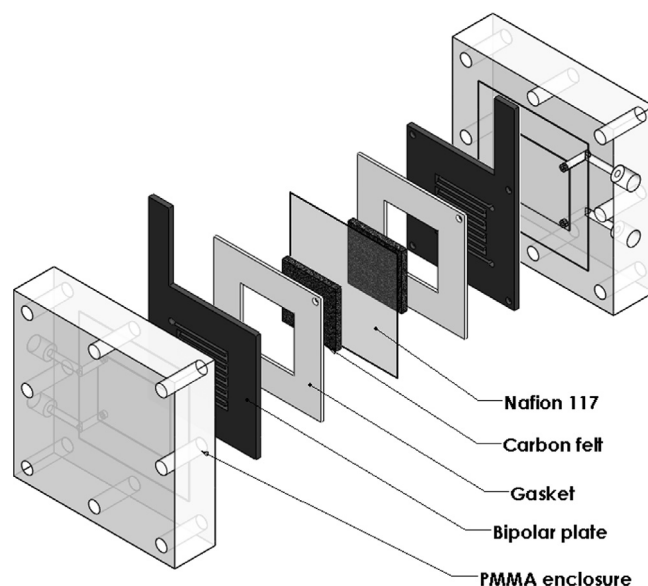


Fig. 1. Schematic of a transparent VRFB.

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