



Reduction of capacity decay in vanadium flow batteries by an electrolyte-reflow method



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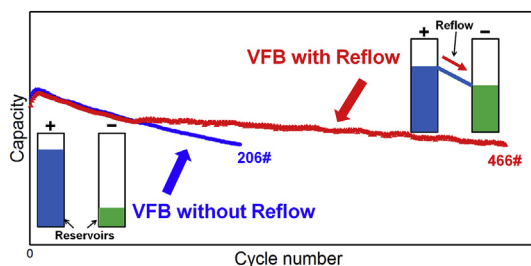
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HIGHLIGHTS

- An electrolyte-reflow method for reducing capacity decay in VFB is presented.
- Different current density and start-up time of the method are investigated.
- With this method, the VFB cycle number increases from 206 to 466 at 160 mA cm⁻².

GRAPHICAL ABSTRACT



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ABSTRACT

Electrolyte imbalance is a major issue with Vanadium flow batteries (VFBs) as it has a significant impact on electrolyte utilization and cycle life over extended charge-discharge cycling. This work seeks to reduce capacity decay and prolong cycle life of VFBs by adopting a novel electrolyte-reflow method. Different current density and various start-up time of the method are investigated in the charge-discharge tests. The results show that the capacity decay rate is reduced markedly and the cycle life is prolonged substantially by this method. In addition, the coulomb efficiency, voltage efficiency and energy efficiency remain stable during the whole cycle life test, which indicates this method has little impact on the long lifetime performance of the VFBs. The method is low-cost, simple, effective, and can be applied in industrial VFB productions.

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1. Introduction

With the aggravation of energy crisis and environmental pollution, large-scale energy storage systems have captured global attention for the increasing demands of the efficient utilization of renewable energy resources [1–4]. Vanadium flow battery (VFB),

first proposed in 1980s, was considered to be one of the most promising large-scale energy storage systems for its numerous advantages, such as long cycle life, low environmental impact, and flexible operation [5–10]. In a VFB, the electrolytes of V²⁺/V³⁺ and VO²⁺/VO₂⁺ in sulfuric acid solution are stored in the negative and positive reservoirs, respectively, and pumped cyclically into a cell where the electrochemical reactions take place [11,12].

The capacity of a VFB is determined by the concentration and volume of the electrolyte, so it can be increased by just adding more electrolytes into the reservoirs. In addition, the issue of cross-

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contamination in other redox flow batteries can be avoided, because four oxidation states of vanadium ions with single element (V^{2+} , V^{3+} , VO^{2+} , VO_2^+) are employed as the active species in both the half-cells (positive and negative). Theoretically, a VFB can obtain high capacity and long service life. However, electrolyte imbalance, which implies the inequality of oxidized and reduced species, is usually found during the charge-discharge cycles of VFBs [11,13,14]. The imbalance occurs primarily due to the transfer of ions and water across the ion exchange membrane (IEM) and side reactions in the cell, giving rise to the decreases in cell performance and energy capacity [15–19]. The transfer of vanadium ions and water, which includes the transfer of vanadium ions with the bound water, the transfer of protons with the dragged water and the transfer of water driven by osmosis, leads to the concentration and volumetric disequilibrium [20]. The subsequent self-discharge reactions occur between vanadium ions experiencing diffusion across the membrane and the native vanadium ions [21]. These processes can be reversed by simple remixing the total electrolyte to recover the lost capacity, but frequent maintenance will limit the application of VFBs. Meanwhile, other side reactions, which include gassing side reactions at both electrodes and air oxidation of bivalent vanadium ion in the negative electrolyte, bring about the symmetrical valence. The two processes above require chemical or electrochemical rebalancing for capacity restoration [13,22].

Progress has been continually made to investigate the mechanism of electrolyte imbalance in VFBs, and how to recover the imbalance. Especially, the transfer behavior of different ions and water across the membrane has been investigated by many researchers. Skyllas-Kazacos's group investigated the behavior of ion diffusion and water transport across the membrane as well as side reactions, proposing several methods of state-of-charge (SOC) monitoring [13,15,21–26]. Zhang's group investigated the transfer behavior of the ions across the membranes and proposed the capacity fade mechanisms of VFBs with different membranes [20,21,27]. The effects of side reactions on electrolyte imbalance were also studied [28–31]. Some parameters of electrolytes were measured to obtain the oxidation state of vanadium and research the electrolyte imbalance. Our group presented online spectroscopic study on monitoring the electrolytes and obtained parameters such as state of charge of the electrolytes [14,32,33]. Amornchai Arpornwichanop et al. introduced a modified open circuit voltage (OCV) and a four-pole cell device to predict the oxidation state of vanadium in the electrolytes [18,34]. Methods of compensation of capacity decay and rebalancing electrolyte were also proposed and discussed. Researchers from Pacific Northwest National Laboratory found that by regulating the pressure difference at each side of the separator, physically transferring a specific amount of the positive electrolyte to the negative reservoir and returning the surplus vanadium ions from the positive side back to the negative side through interdiffusion, can all reduce capacity fade [35,36]. A.H. Whitehead et al. proposed a novel method of reacting the evolved H_2 with the charged positive electrolyte to hinder the charge imbalance [37]. E.C. Kumburet al. investigated the operation of a VFB under asymmetric current condition to reduce its capacity fade [38].

In our previous studies, we have focused on the modification of membranes and the graphite felt, investigation into the Nafion membrane pretreatment, and study on the on-line monitoring and stability of electrolyte [14,32,33,39–45]. In this work, a method is developed to reduce capacity decay and prolong cycle life in VFBs by guiding the electrolyte from one reservoir to reflow automatically and periodically into the other reservoir through a connector, without changing the operation condition. Compared with other conventional experimental and theoretical methods, the proposed method is low-cost, simple, effective, and can be applied in

industrial VFB productions.

2. Experimental section

2.1. Electrolyte-reflow mechanism

The electrolyte-reflow mechanism is illustrated in Fig. 1(a). As to Nafion membrane, the net vanadium ions and water transfer occurs from the negative to the positive half-cell [17,20], so the volume of the positive electrolyte increases and the volume of the negative electrolyte decreases after each cycle. The first row in Fig. 1(a) shows the volume change in a regular VFB with Nafion membrane (green bars in Fig. 1(a)) during charge-discharge cycles. Before pre-charge, the electrolytes in the positive and negative reservoirs (blue bars in Fig. 1(a)) have the same level (the yellow lines in Fig. 1(a)). As cycling proceeds, the volume of the electrolyte in the positive reservoir keeps increasing and the volume of the electrolyte in the negative reservoir keeps decreasing. At last, nearly all the electrolytes in the negative reservoir of the regular VFB transfer into the positive side across the membrane, and the VFB cannot be used any more before rebalancing the electrolytes. In order to solve the problem of volumetric disequilibrium, we connect the two reservoirs with a connector (the orange lines in Fig. 1(a)). Then the increasing electrolytes on the positive side of the VFB can reflow into the negative side. The second row in Fig. 1(a) shows the volume

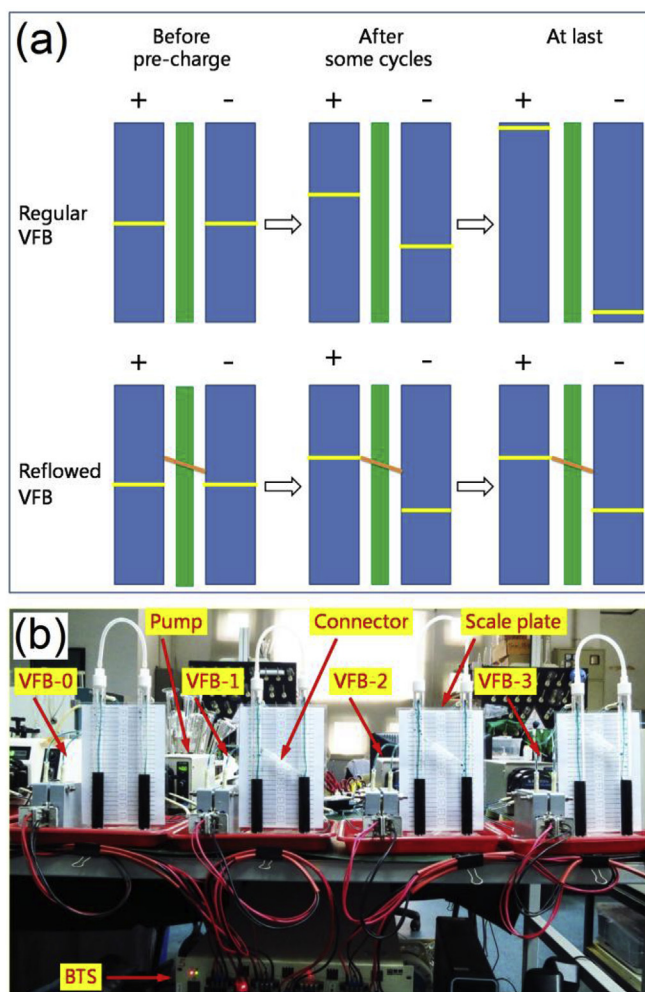


Fig. 1. (a) Schematic representation of the electrolyte-reflow method; (b) Photograph of the cycle life test system.

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