

The benefits and limitations of electrolyte mixing in vanadium flow batteries



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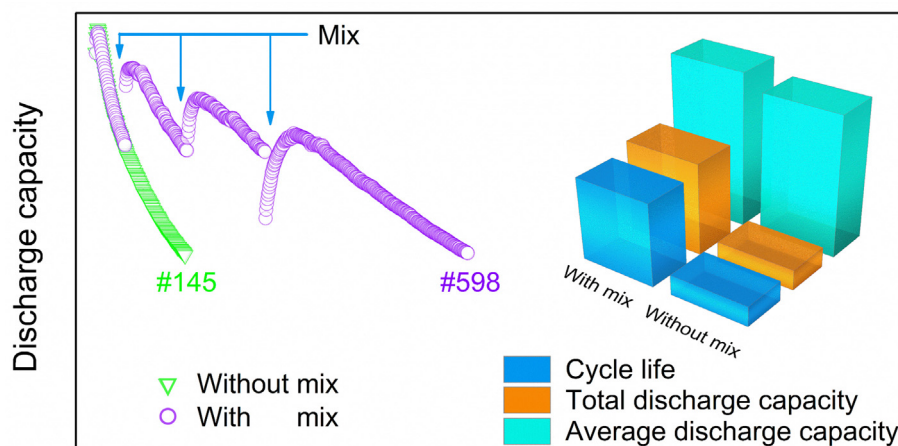
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HIGHLIGHTS

- The benefits and limitations of electrolyte mixing method are studied in this work.
- Different current densities and mix times are studied.
- The VFB cycle number increases from 145 to 598 at 160 mA cm⁻² by mixing the electrolytes.

GRAPHICAL ABSTRACT



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ABSTRACT

Cycle life prolongation and discharge capacity regeneration have drawn enormous attention in the field of vanadium flow batteries (VFBs). Among all the methods, mixing the positive and negative electrolytes is the most efficient, but the study about the proper time and the effect of the mix method is relatively deficient. In this study, different mix times and current densities are chosen to explore the benefits and limitations of the mix method, also the mechanism of discharge capacity behavior is discussed. Through the mix method, not only the cycle number has been extended significantly, but also the voltage and energy efficiencies are recovered. Although the contribution of the mix method is restrained by the average valence of the mixed electrolytes, it can be alleviated by electrolysis. The mix method is economic, uncomplicated and can be employed in industrial applications.

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1. Introduction

Under the increasing pressure of population expansion and energy crisis, it is highly desirable to develop the utilization of

renewable energy sources. As electrical energy storage (EES) plays a crucial role in the application of renewable energy sources and serves as a connection between the current electricity grid and fluctuating non-fossil energy sources, tremendous efforts have been made in the exploration of techniques for EES in recent years [1–6]. Proposed by NASA in 1970s, redox flow battery (RFB)

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attracts considerable attention due to its good safety, fast response and separate design in power and energy [2,7–11].

To date, all-vanadium redox flow battery (VFB, VRB or VRFB), suggested by M. Skyllas-Kazacos and co-workers in 1980s [12], is regarded as one of the most promising large-scale energy storage systems for its long cycle life, flexible design, high efficiency and relatively low environmental impact [6,9,13–19]. Furthermore, the VFB system has been commercialized as a large-scale energy storage system [20,21]. Also, the technology, finance and policy aspects have been demonstrated [22]. In a VFB, the positive electrolyte ($\text{VO}^{2+}/\text{VO}_2^+$ in sulfuric acid solution) and the negative electrolyte ($\text{V}^{2+}/\text{V}^{3+}$ in sulfuric acid solution) are reserved in the positive and negative reservoirs respectively, and are pumped into the cell stack to take part in electrochemical reactions [8,23]. Theoretically, VFB has a long cycle life, but it suffers severe capacity loss and performance degeneration, which is mainly resulted from electrolyte imbalance. The electrolyte imbalance is mainly caused by water and vanadium ions transfer through the separator as well as parasitic side reactions [24–26]. Owing to different permeability of vanadium ions with various oxidation states, non-equilibrium transfer of cations causes vanadium concentration imbalance in the positive and negative electrolytes. Meanwhile, difference between the chemical composition of the positive and negative electrolytes brings non-equilibrium transfer of water [27], leading to colossal volume change. Furthermore, V^{2+} , V^{3+} , VO^{2+} and VO_2^+ ions permeate through the separator with different number of bonded water molecules [15], aggravating the non-equilibrium transfer of water. In addition, side reactions including gas evolution, oxidation of V^{2+} ions by oxygen and precipitation formation of V_2O_5 endow the electrolyte imbalance by consuming electrons and available vanadium ions. Thus significant capacity loss and battery performance degeneration occur.

With such issues, there is emphasis on reducing the capacity decay rate of VFB. Thus pioneering studies about the mechanism of capacity decay and electrolyte composition change during the charge–discharge cycling process have been achieved, including water transfer and permeation of vanadium cations through membranes [27–30], thermal and dynamic modelling of battery configuration, self-discharge reactions, ion diffusion and side reactions [31,32], and the effects of electric field on ion crossover [33]. Together with working on the capacity decay mechanism, some advanced technologies have been employed to detect the component changes of electrolyte during the charge–discharge cycling process by monitoring state of charge (SOC) [34–36], transfer of active materials [37,38], oxygen evolution [39] and hydrogen evolution behaviors [40]. With the knowledge of theoretical modelling and virtual monitoring, it is easy to conclude that mitigating the ion transfer rate is one of the most efficient choices to reduce capacity decay rate. Hence, highly ion-selective separators have been suggested [41–47]. Although the rate of capacity decay can be alleviated significantly by the highly ion-selective separators, the non-equilibrium transfers of water and vanadium ions still exist, leading to electrolyte imbalance ultimately. To this end, burgeoning explorations have been made in operational conditions to regenerate capacity of VFB, such as tuning the sap pressure of the positive and negative electrolytes [48], employing asymmetric positive/negative electrolyte volumes [49], balancing the osmotic pressure of the electrolytes [50], altering the charging and discharge currents [51] and reflowing the electrolytes from the positive side to the negative side [52].

In the exploration process of regenerating discharge capacity, it is noteworthy that VFB system is free from cross-contamination as all the active materials are vanadium ions in the positive and negative electrolytes. This brings the possibility to regenerate VFB capacity by mixing the positive and negative electrolytes [8,53]. Although the mix method is uncomplicated and efficient, the study

on the proper time of mix and the practical application value of mix method is relatively deficient. In this paper, the effect of mix method is studied, the benefits and limitations for prolonging battery cycle number are explored, and the mechanism of discharge capacity retention behavior is discussed. Comparing with other presented operational methods, the mix method studied in this paper is uncomplicated and economic.

2. Experimental section

2.1. Test system and parameter

The cycle number test system applied in this study was based on our previous works [54,55]. The digital photos and the schematic diagrams of a typical VFB system tested in this study are displayed in Fig. 1. Reservoirs, tubes, cells, flow controllers, peristaltic pumps and flow cuvettes were employed. The cell of the VFB contained two graphite polar plates (60 mm × 60 mm × 3 mm, Shanghai Hongfeng Industrial Co., Ltd), two pieces of graphite felts (50 mm × 50 mm × 5 mm, Gansu Haoshi Cabon Fiber Co., Ltd) and a Nafion 115 membrane (70 mm × 70 mm, Dupont). The graphite felts were washed in 50% ethanol solution, deionized water and then heated in the air at 420 °C for 10 h to improve hydrophilicity and electrochemical behavior. Nafion 115 membranes were treated in 3 wt% H_2O_2 solution, deionized water, 1 M H_2SO_4 solution and deionized water for 1 h in sequence. Flow cuvette was homemade with absorption depth of 1 mm. The positive and negative electrolytes containing 1.5 M vanadium ion ($\text{V}^{3+}/\text{VO}^{2+} = 1:1$) and 2.0 M free H_2SO_4 were 50 mL in all reservoirs initially. The peristaltic pump (BT 100 M, Baoding Chuangrui Precision Pump Co., Ltd) was used to control the flow rate of the positive and negative electrolytes at 60 mL min^{-1} . A battery test system (BTS CT-3008W, 5V6A, Neware Co., Ltd) performed the cycle number test in the voltage window of 1.65–0.80 V to avoid electrochemical corrosion on graphite polar plates and graphite felts. All the VFBs in this study were tested simultaneously under the same condition to exclude systematic error.

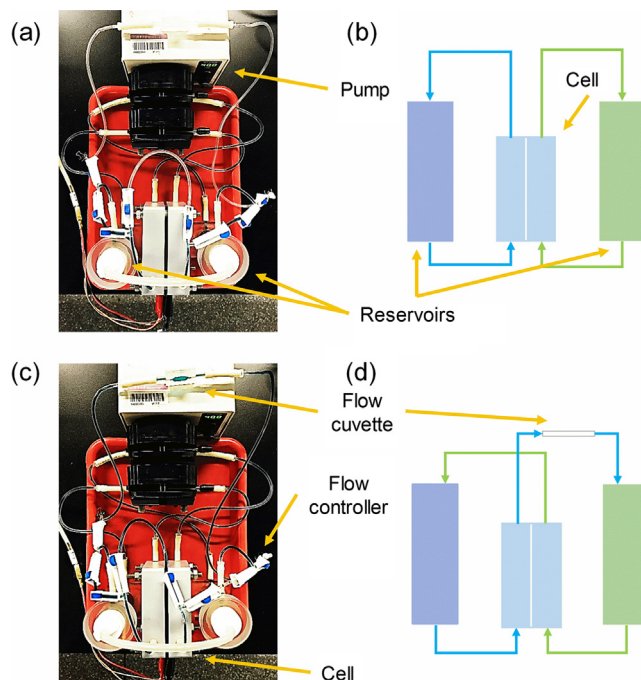


Fig. 1. (a, c) The photos of the normal work process and the mix process; (b, d) The schematic diagrams of the normal work process and the mix process.

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