Improved electrochemical performance for vanadium flow battery by optimizing the concentration of the electrolyte

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HIGHLIGHTS

- This work is developed based on physical property, half-cell and cell performance.
- Electrolyte of 1.6 M $VOSO_4$ and 2.8 M H_2SO_4 exhibits the best performance.
- This work can provide direct guidance to the engineering application of VFB.

ABSTRACT

In order to improve the utilization rate of the electrolyte and further reduce the energy storage cost, the physicochemical properties, electrochemical characteristics and charge/discharging behaviors of VFB with different concentration of $VOSO_4$ and H_2SO_4 were investigated systematically. The physicochemical characterizations show that the viscosity increases with the increasing concentration of $VOSO_4$ and H_2SO_4, and the conductivity increases with the increasing concentration of H_2SO_4 while decreases with the increasing concentration of $VOSO_4$. Both CV and EIS results demonstrate that the electrolyte with 1.6 mol L^{-1} $VOSO_4$ and 2.8 mol L^{-1} H_2SO_4 presents the best electrochemical performance because of the coupling effect of the viscosity, conductivity and electrochemical activity. Different with the half-cell electrochemical tests, the battery performance of VFB is not only dependent on the electrochemical activity of electrode/electrolyte interface, but also closely related to the conductivity of electrolyte and diffusion rates of the active particles between anolyte and catholyte. Taking the battery efficiencies and capacity into consideration, VFB with 1.6 mol L^{-1} $VOSO_4$ and 2.8 mol L^{-1} H_2SO_4 exhibits the optimal electrochemical performance. The accomplishment of this work not only gives data support to the fundamental research of VFB, but also provides theoretical direction to the engineering application of VFB.

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1. Introduction

With the continually growing environmental pollution and energy crisis, the sustainable energy sources such as solar and wind have been rapidly developed last decades. However, it is necessary to assort with a large-scale energy storage system during the renewable energy power generation because of their variable and intermittent characteristics [1]. The redox flow battery (RFB), which possesses the advantages of the long cycle life, deep charge capacity

and flexible design, attracts more attentions than other conventional secondary batteries among the potential energy storage technologies [2]. In particular, the all vanadium flow battery (VFB), which uses the V(II)/V(III) and V(IV)/V(V) redox couples as the negative and positive half-cell electrolytes, and the proton exchange membrane as the separator, not only presents a high reliability, but also minimizes the possible cross-contamination of the half-cell electrolytes, indicating a great promise for large-scale energy storage applications [3,4].

Up to now, the application of VFB in the energy storage demonstration project is worldwidely developed and its installment capacity is more than 20 MW [4]. However, compared with

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the price of the stored electrical energy, the excessive energy storage cost limits the commercial application of VFB. The electrode materials, membrane and electrolytes are the key components for VFB and their costs account for the majority of the overall cost. Therefore, aiming to the key materials, there are mainly three approaches to reduce the overall cost of VFB, such as the modification of the electrode materials, improvement of the composition and structure of the membrane, optimization of the electrolyte compositions. First of all, considerable efforts have been devoted to improving the electrochemical performance of the electrode materials by increasing their surface oxygen or nitrogen content such as the heat treatment, acid treatment and plasma treatment, etc [5−9]. To provide more active cites, the transition metals and/or their oxides such as Pb [10], Bi [11], W [12], Mn [13] were modified on the carbon nanofibers by chemical impregnation or vapor deposition method. Secondly, some pioneers focused on the optimization of the separator for VFB and prepared the composite membrane with sandwich structure [14]. The concepts of the polyvinylidene fluoride membrane (PVDF) and non-fluorinated membrane especially for the anion exchange membrane were also proposed to reduce the high-cost of the separator [15,16]. Thirdly, the influences of the organic and inorganic additives and the mixed-acid system of H_2SO_4−HCl on the electrochemical activity toward to the vanadium redox couples, in addition to the stability of the electrolytes in the relatively harsh environment were also researched [17−19]. Moreover, the preliminary studies of the concentration optimization of the electrolytes were also developed from the point of the thermodynamic stability or electrochemical kinetics [20,21]. Definitely, the above-mentioned research results are of great significance to deepen the insight of the reaction process for VFB, whereas the energy storage cost for VFB is still relatively higher than that of other energy storage technologies because of the lack of the feasible technology for mass production.

With the consideration of the highly decoupled battery stack and active electrolyte, the concentration optimization of the electrolyte for VFB will be more simple and effective for the reduction of the energy storage cost. In general, the higher concentration of the vanadium ions in the electrolyte, the larger energy density for the VFB stack, however, considering the possible precipitation of V(V) ions at a higher temperature [22], as well as the higher viscosity for the concentrated electrolyte, the concentration of the vanadium ions in the electrolyte used in the demonstration project of VFB is about 1.5−2.0 mol L^{-1} [21]. In addition, the matching relationship between the vanadium and H_2SO_4 concentration is of great importance for increasing the stability and energy efficiency of vanadium electrolyte [20]. Nevertheless, there is little in-depth and systematic study on the optimal concentration ratio between the vanadium ions and H_2SO_4, in spite of the strong influence of the electrolyte compositions and their concentrations on the electrochemical performance for VFB, which resulted in the lack of the data support for the engineering application. Therefore, it is necessary to systemically investigate the effect of the concentration optimization on the battery performance and consequently the energy storage cost for VFB will be further reduced with half effort.

In the previous work, the temperature-related reaction kinetics of the VO_2^+/VO^{2+} redox couple on a graphite electrode in sulfuric acid solutions has been investigated and two diffusion equations for both VO_2^+ and VO^{2+} ions in sulfuric acid solutions have been established [23]. Herein, a more detailed study of the favorable proportion of vanadium and H_2SO_4 was undertaken to determine the optimum electrolyte composition and their concentration for VFB through the physical property characterization, electrochemical measurement and the charge-discharge test. At last the optimal concentration ratio of vanadium ions and H_2SO_4 is summarized with a comprehensive consideration according to the above-mentioned test results.

2. Experimental

2.1. Preparation of the electrolytes

All chemicals used in the present experiments were analytically pure agents and all solutions were prepared with de-ionized water. The electrolytes of the blended $VOSO_4$ and H_2SO_4 solution with various concentration were prepared by dissolving $VOSO_4 \cdot nH_2O$ (n = 3.0162, Shanghai Huating Chemical Co. Ltd., China) in concentrated H_2SO_4 solution and then quantitatively diluted with the deionized water and dilute H_2SO_4 solution to produce the electrolytes with different H_2SO_4 and $VOSO_4$ concentrations. Taken the consideration of the stability for the vanadium electrolytes during the normal working temperature range of 5−45 °C [20−22,24,25], the concentration of $VOSO_4$ have been controlled between 1.4 and 2.2 mol L^{-1}, as for the H_2SO_4, its concentration is in the range of 2.2−3.4 mol L^{-1}.

In addition, the measurements of pH for the concentrated and dilute H_2SO_4 solutions were performed with a pHS-25 pH meter after the quantitative dilution (Shanghai Precision Instrument Co. Ltd, China).

2.2. Physical characterizations of the electrolytes

The viscosity of the blended $VOSO_4$ and H_2SO_4 solution with different concentration was measured with the Ubbelohde viscometer at 293 K. The electrical conductivity of these electrolytes was also determined using a conductivity meter (Shanghai REX Instrument Factory, China) at 293 K.

2.3. Electrochemical measurements

In order to evaluate the effect of the concentration of the active reactants in the electrolytes on the electrochemical performance, the electrochemical measurements were performed using the Reference 600 electrochemical workstation (Gamry Instruments, USA) with a three-electrode system. A pyrolytic graphite electrode (PGE) with the area of 0.1256 cm^2 purchased from Wuhan Gao-ss Union technology co., LTD and a 1 cm^2 platinum sheet were used as the working electrode and counter electrode respectively, a saturated calomel electrode along with a salt bridge full of saturated potassium chloride solution was used as reference electrode. Prior to each measurement, the PGE was polished on the given polishing cloth and then ultrasonic cleaning in distilled water for 1 min, at last washed with distilled water. All potentials reported here were referred to SCE.

The electrochemical property of the different electrolytes was tested by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests. The CV and EIS curves were firstly recorded in 2.5 mol L^{-1} H_2SO_4 solution with varying contents of $VOSO_4$, the concentration of which is 1.4, 1.6, 1.8, 2.0 and 2.2 mol L^{-1}, respectively. And then the similar tests were performed in 1.6 mol L^{-1} $VOSO_4$ solution with varying contents of H_2SO_4, the concentration of which is 2.2, 2.5, 2.8, 3.1 and 3.4 mol L^{-1}, respectively. The CV behaviors of PGE in different electrolytes were investigated within range of 0−1.5 V at a scan rate of 5 mV s^{-1}. In addition, the specific CV characteristic of PGE in 1.6 mol L^{-1} $VOSO_4$ and 2.8 mol L^{-1} H_2SO_4 solution was evaluated within range of 0.3−1.5 V at different scan rates. The EIS tests were measured by applying an alternating voltage of 5 mV over the frequency ranging from 10^5 to 10^{-2} Hz and the corresponding results were fitted with a simplified equivalent circuit model.