



Investigations on the self-discharge process in vanadium flow battery



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HIGHLIGHTS

- The diffusion coefficients of vanadium ions were in order of $V^{2+} > VO^{2+} > VO_2^+ > V^{3+}$.
- The self-discharge behavior of VFB was investigated in detail for the first time.
- Nafion 115 was selected to investigate the self-discharge behavior.
- The experiment was done under argon to eliminate the influence of oxygen.
- The mechanism was clarified during self-discharge process.

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ABSTRACT

The self-discharge process of vanadium flow battery (VFB) assembled with Nafion 115 is investigated in very detail for the first time. The self-discharge phenomenon of VFB is closely related to the diffusion coefficients of the vanadium ions, which are found to be in the order of $V^{2+} > VO^{2+} > VO_2^+ > V^{3+}$. Five regions on the change of open circuit voltage (OCV) are clearly found during the self-discharge process. The regions include three platforms and two obvious decreasing regions. VO_2^+ disappears in the second region, while the V^{2+} disappears in the fourth one. In the first three regions, the self-discharge reactions at the positive and negative side are different, owing to the crossover of vanadium ions. In the last two regions, the changes of vanadium ions are derived from the diffusion of V^{3+} and VO^{2+} at positive and negative electrolyte. The self-discharge process at different flow rates or different state of charge (SOC) is also investigated, indicating that the self-discharge time shortens with increasing of flow rate between 40 and 80 mL/min or decreasing of the initial SOC. This paper will provide very valuable information for the relaxation or elimination of self-discharge phenomenon of VFB, which is one of the most troublesome issues in VFB application.

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1. Introduction

Renewable energy sources like solar power and wind power attracted more and more attention due to the critical issues of energy shortage and air pollution [1–3]. However, the renewable energy sources are instable and discontinuous, they need to be combined with a large-scale energy storage device to realize their smooth output and to improve their stability [1,4,5]. A vanadium

flow battery, which was invented by Skyllas-Kazacos and co-workers in 1980s [6,7], is one of the most suitable candidates for the large-scale energy storage, owing to its attractive features like high energy efficiency, long cycle life, high safety and environmentally friendly, etc [8–11].

So far, many VFB demonstrations have been carried out in different fields, which proved the promising features of VFB. However, there are still some critical issues need to be clarified. Among all the issues, the self-discharge phenomenon of the VFB stacks is one of the most critical problems. Especially for the backup power, the self-discharge will seriously affect the backup time and final battery performance. However, the real mechanism of self-discharge in VFB was not very clear yet, only part of research was focused on the self-discharge process.

It is well known that the different diffusion vanadium ions from

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one half-cell to the other will induce self-discharge reactions, and further lead to an imbalance between the SOC of the two half-cell electrolytes and a subsequent drop in capacity [12]. You et al., established a simple mathematical model to predict the self-discharge process in a kilowatt-class vanadium redox flow battery stack [13]. Even though, very seldom research was carried out to systemically investigate the detailed mechanism of self-discharge in a VFB, which is very important for a VFB system. In addition, an overwhelming majority of the current researches were accomplished under the atmosphere or with the protection of inert gas like nitrogen or argon [14]. In this case the V^{2+} ions can be easily oxidized even at very low concentration of oxygen gas [15], which makes the results more confusing. In this article, the mechanism self-discharge will be investigated in detail under the oxygen-free condition.

In this paper, Nafion 115 is selected as a membrane for the self-discharge experiment under VFB operating condition. The effect of flow rate or initial SOC on self-discharge process is investigated as well. Besides, the permeability of different vanadium ions across a Nafion 115 was detected using a diffusion cell. To eliminate the influence of oxygen, all the experiments were carried out in a glove box with 99.999% argon.

2. Experiments

2.1. The preparation of the vanadium electrolyte and membrane treatment

The vanadium electrolyte was prepared by dissolving $VOSO_4 \cdot 4H_2O$ (Haizhongtian Fine Chemical Factory, Shenyang) in 3 M sulfuric acid (Kemio Chemical Reagent Co. Ltd, Tianjin) to form a 1.7 M solution. The V (II), V (III) and V (V) electrolytes was prepared from V (IV) electrolyte via an electrolytic cell. V (IV) electrolytes with volume ratio of 2/1 were added into positive and negative side respectively. Then the cell was charged to theoretical capacity to prepare 1.7 M V (V) and 1.7 M V (II) respectively, the current density is 80 mA cm^{-2} and then gradually decrease to 10 mA cm^{-2} . While V (III) was prepared by oxidation of V (II).

75% SOC of electrolyte was prepared by charging the above cell to 75% of theoretical capacity.

In addition, the Nafion 115 membranes (Du Pont Company, CEM) were pretreated before the experiments. The membranes were first boiled in a 3% H_2O_2/H_2O solution of hydrogen peroxide, followed by rinsing in boiling distilled water. Then the membranes were boiled in a 1 mol L^{-1} sulfuric acid solution and finally washed with boiling distilled water. The time of each treatment was 1 h [16].

2.2. The permeability of different vanadium ions across Nafion 115

The permeability of vanadium ions was detected by using a diffusion cell, as described earlier [17]. The diffusion cell was separated by a membrane. The left cell was filled with 1.7 M vanadium ions with different valences in 3 M H_2SO_4 solution, while the right one was filled with the mixture of $MgSO_4$ and H_2SO_4 in order to equalize the ionic strengths and to minimize the osmotic pressure effect before the test of vanadium permeability. Both sides were vigorously stirred by magnetic stirrers to avoid concentration polarization. Samples from the right cell were collected at regular time interval. The concentration of vanadium ion was detected by using UV–Vis spectrometer.

2.3. The self-discharge experiment of Nafion 115

A single VFB was employed to investigate the self-discharge process. A single VFB cell was assembled by sandwiching a

membrane between two carbon felt electrodes, clamped by two graphite polar plates. The effective area of electrode was 48 cm^2 . Nafion 115 was selected as ion exchange membrane, carbon felts were used as electrodes. The original volume of the electrolytes at each side was 100 mL. And the electrolyte was reserved in graduated cylinder. The state of VFB was kept at open circuit and the electrolytes were cycling pumped into the cell by peristaltic pump (BT 100M, Baoding Chuangrui Precision Pump Co. Ltd) during self-discharge process. The flow rate of electrolyte was controlled in the range between 40 and 80 mL/min. The self-discharge performances of the VFB were conducted by using a charge–discharge controller (Model BT 2000, Arbin Instruments Corp., USA). The open circuit voltage of VFB was recorded by the charge–discharge controller till the voltage was lower than 0.08 V.

The volume change of positive and negative electrolyte during discharge process was recorded at a regular time interval, meanwhile, a 0.5 mL sample was collected from the positive and negative electrolyte at a regular time interval, respectively. The concentration of vanadium ions with different valences was measured via auto potentiometric titrator (905 titrando, Metrohm, Switzerland). The sample was titrated by using standard potassium permanganate solution as titrant and mixed acid (sulphuric acid and phosphoric acid) as medium. The titration finished when the potential saltation appeared. And the vanadium concentration was calculated by the volume of standard potassium permanganate solution corresponding to the potential saltation.

3. Results and discussion

3.1. The permeability of different vanadium ions across Nafion 115

The vanadium ions could transfer across Nafion 115 from enrichment side to deficiency side under the drive force of concentration. The diffusion coefficient of vanadium ion across the membrane abides by the Fick law:

$$V_B \frac{dC_B(t)}{dt} = A \frac{P}{L} (C_A(t) - C_B(t)) \quad (1)$$

where V_B is the volume of electrolyte at deficiency side (L); C_A is the concentration of vanadium ions at enrichment side ($\text{mol} \cdot \text{L}^{-1}$); C_B is the concentration of vanadium ions at deficiency side ($\text{mol} \cdot \text{L}^{-1}$); A is the effective area of the membrane (m^2); P is the diffusion coefficients of vanadium ions ($\text{m}^2 \cdot \text{s}^{-1}$); L is the thickness of the membrane (m); t is the test time (s). C_B is vanadium ion

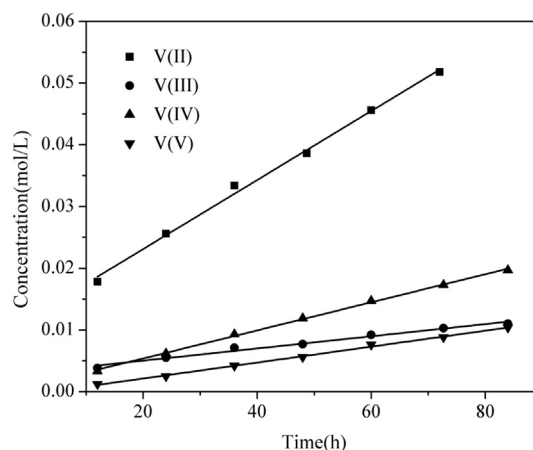


Fig. 1. The concentration of vanadium ions with different valence at different time at the deficiency side.

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