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The transfer behavior of different ions across anion and cation exchange membranes under vanadium flow battery medium

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HIGHLIGHTS

- The transfer behavior of different ions across membrane was investigated in VFB.
- VX-20 and Nafion 115 were selected to investigate the transfer behavior.
- The capacity fade mechanisms of different membranes were investigated.

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ABSTRACT

The transfer behavior of different ions (V^{2+}, V^{3+}, VO^{2+}, VO_2^+, H^+, SO_4^{2-}) across ion exchange membranes is investigated under vanadium flow battery (VFB) operating condition. VX-20 anion exchange membrane (AEM) and Nafion 115 cation exchange membrane (CEM) are selected to investigate the influence of fixed charged groups on the transfer behavior of different ions. The interaction between different ions and water is discussed in detail aiming to ascertain the variation of different ions in the charge–discharge process. Under the VFB medium, the transfer behavior and function of different ions are very different for the AEM and CEM. V^{2+} ions at the negative side accumulate when VFB is assembled with Nafion 115, while the VO_2^+ ions at the positive side accumulate for VX-20. The SO_4^{2-} ions will transfer across Nafion 115 to balance the charges and the protons can balance the charges of VX-20. Finally the capacity fade mechanism of different membranes is investigated, showing that the capacity decay of VFB assembled with Nafion 115 mainly results from the cross mix of vanadium ions across the membrane, however, for VX-20, the side reactions can be the major reason. This paper provides important information about electrolyte for the application of VFB.

1. Introduction

Renewable energy sources such as solar and wind power have attracted global attention, due to the current critical issues of energy shortage and air pollution. [1–3] However, these instable and discontinuous renewable energies need to be combined with large-scale energy storage to improve their stability and to realize their stable output. Thus, large-scale energy storage becomes the key technology that realizes the wide application of renewable energies. [1,4].

The vanadium flow battery (VFB), which is firstly proposed by Maria Skyllas-Kazacos and co-workers in 1985 [5,6], has been regarded as one of the most competitive candidates for the large-scale energy storage [7], owing to its high energy efficiency, long cycle life, high safety and environmentally friendly, etc. [8–12].

In a VFB, the power rate and energy can be designed independently. Its power rate is determined by the electrode area and the number of the VFB single cells, while, its energy can be controlled by the volume and concentration of vanadium electrolytes. The transfer behavior of electrolytes plays an significant role in determining the VFB performance, especially the capacity decay. For example, the diffusion of vanadium ions across the membrane will lead to the self-discharge and side reactions at the positive and negative sides, which further affects the VFB capacity over long-term charge–discharge cycling. [12,13] Maria Skyllas-Kazacos and co-workers investigated the water transfer behavior across CEMs and found that the direction of preferential water transfer is dependent on the state of charge (SOC) of the vanadium

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electrolytes. [14] Later on, transfer behavior of different vanadium ions across the membranes during charge and discharge was investigated as well. Concentration profiles of the different vanadium ions have been modeled in order to predict expected capacity loss over extended charge–discharge cycling. [15] However, the VFB medium is very complex [7], different ions like vanadium ions, sulfates ions and protons coexisted in the electrolyte, the interaction between them and water is obscure so far. At the same time, the state of vanadium electrolyte and the transfer behavior of different ions are closely related to the ion exchange membranes, the characteristics of membranes, e.g. the functional charged groups, the backbone, the micro structures, will greatly affect their transfer behavior. [8,16,17] However, the current research is mostly related perflourinate CEMs [14], seldom research was focused on AEMs. In addition, an overwhelming majority of the researches about vanadium electrolyte was accomplished under the atmosphere with the protection of inert gas like nitrogen or argon [18], even though, the V^{2+} ions can be easily oxidized even at very low concentration of oxygen [19], which makes the results more confusing. In this article, the glove box with 99.999% argon and less than 1 ppm oxygen is used to eliminate the influence of oxygen.

To understand the change of different ions in the charge–discharge process, two kinds of membranes with different ion exchange groups (Nafion 115 CEM and VX-20 AEM) were selected to investigate the transfer behavior and of different ions across them in detail. The changes of different ions in electrolyte were detected during charge–discharge process, and the transfer behavior of different ions was thorough discussed as well. The article fully invesitiaged the different ions change phenomena in VFBs sandwiched with Nafion 115 and VX-20, respectively. Moreover, the primary reason of the capacity decay of VFB assembled with Nafion 115 or VX-20 as membrane was investigated.

2. Experimental section

All experiments described below were done in the glove box with 99.999% argon and less than 1 ppm oxygen. All experiments described below were done at 25 °C and under the standard atmospheric pressure. All the measurements were based on at least three samples, and the average values were used. The standard deviation on the measurements is about 5%.

A VFB single cell was employed to investigate the transfer behavior of water, vanadium ions, sulfate ions and protons during charge–discharge. The VFB cell was assembled with a membrane between two carbon felt electrodes, clamped by two graphite polar plates. The active area of electrode was 48 cm^2. Nafion 115 (DuPont company, CEM) and VX-20 (Fumatech company, AEM) were selected as ion exchange membranes. The original volume of the electrolytes at each side was 100 mL containing 1.7 M VO^{2+} in positive electrolyte and 1.7 M V^{3+} in negative electrolyte. The volume of positive and negative electrolytes at the end of discharge process was recorded during operation of the VFB. A 2 mL sample was collected from the positive and negative electrolyte, respectively, at the end of a discharge process in a different cycle for further analysis. The charge–discharge performance of the VFB was conducted by using a charge–discharge controller (Model BT 2000, Arbin Instruments Corp., USA). The upper limit voltage of charge was 1.55 V, the lower limit voltage of discharge was 1.0 V. The current density was kept at 80 mA cm^{-2}.

The concentration of vanadium ions with different valences was measured via auto potentiometric titrator (Mettler Toledo, T50) by using standard potassium hypermanganate solution as titrant. The concentration of sulfate ions was measured by method of precipitation, the barium chloride solution was used as precipitant. The concentration of protons was measured by acid-base titration and standard sodium hydrate solution as titrant.

The permeability of vanadium ions was detected using a diffusion cell, as described earlier. [20] The diffusion cells were 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 effects 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 ions was characterized by using auto potentiometric titrator and UV–Vis spectrometer.

3. Results and discussion

3.1. The transformation of the water in electrolyte

To investigate the water transformation across the different kinds of membranes, the electrolyte volume was recorded at the end of a discharge process in a different cycle. Fig. 1 shows the change of electrolyte volume in the positive and negative half-cells when using Nafion 115 and VX-20 as membranes respectively. For Nafion 115, the electrolyte volume increases at the positive side and decreases at the negative side as cycle proceeding. The electrolyte transfers obviously during the first 10 cycles, then, the electrolyte volume hardly changed. However, for VX-20 AEM, the volume of electrolyte at positive side first increases then decreases during the cycle test, and the changing tendency is opposite at the negative side, indicating the transfer direction of water changed from “negative-to-positive” to “positive-to-negative” during the operation of the VFB. This phenomenon is possibly closely related to the transfer behavior of protons, which will be discussed later.

3.2. The transformation of vanadium ions in electrolyte

The vanadium ions normally could transfer through the ion exchange membranes during the operation of a VFB. [13] To investigate the change of vanadium ions in the electrolyte during the VFB operation, the samples were withdrawn from the positive and negative electrolyte at the end of a discharge process in different cycles and the concentration of vanadium ions with different valences was detected.

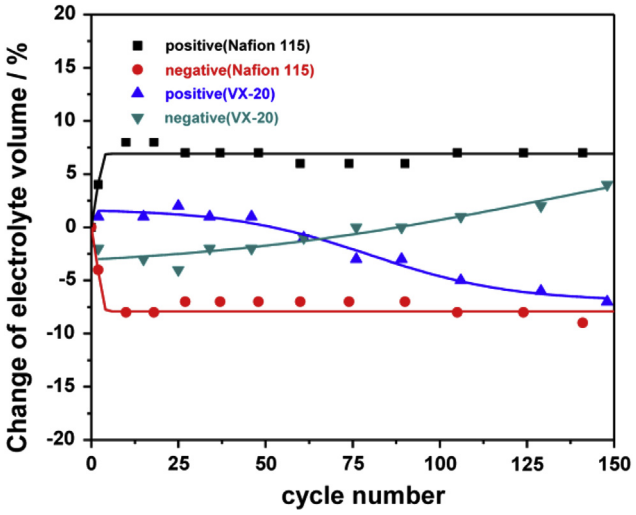

Fig. 1. Change of electrolyte volume in the positive and negative half-cells during cycle process when using Nafion 115 or VX-20 as membrane.