



In-situ investigation of vanadium ion transport in redox flow battery

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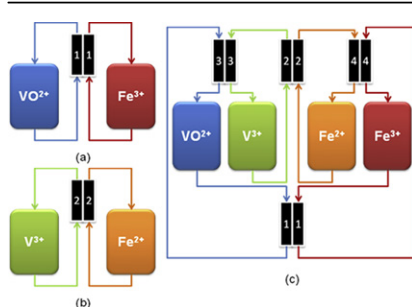
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HIGHLIGHTS

- In-situ study of the transport behavior of V ions during flow battery operation.
- $\text{VO}^{2+}/\text{VO}_2^+ \parallel \text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+} \parallel \text{V}^{3+}/\text{V}^{2+}$ flow batteries were constructed for in-situ measurement.
- A simplified mathematical model to simulate the vanadium ion transport.

GRAPHICAL ABSTRACT



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ABSTRACT

Flow batteries with vanadium and iron redox couples as the electroactive species are employed to investigate the transport behavior of vanadium ions in the presence of an electric field. It is shown that the electric field accelerated the positive-to-negative and reduced the negative-to-positive transport of vanadium ions in the charging process and affected the vanadium ion transport in the opposite way during discharge. In addition, a method is designed to differentiate the concentration-gradient-driven vanadium ion diffusion and electric-field-driven vanadium ion migration. A simplified mathematical model is established to simulate the vanadium ion transport in real charge–discharge operation of the flow battery. The concentration gradient diffusion coefficients and electric-migration coefficients of V^{2+} , V^{3+} , VO^{2+} , and VO_2^+ across a NAFION[®] membrane are obtained by fitting the experimental data.

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1. Introduction

The demand for stationary energy storage has rapidly changed the worldwide landscape of energy system research [1,2], which has brought redox flow battery technology into the spotlight in recent years because it can provide large-scale energy storage to support a more intelligent, efficient, and capable electrical grid system [3,4]. Redox flow battery (RFB) systems are hailed as one of

the most promising technologies to be utilized not only for integrating renewable energy resources, but also to improve the efficiency of grid transmission and distribution. Among the different RFB systems, the all-vanadium redox flow battery (VRB) is probably the most promising and extensively researched flow battery system [5–8]. Capitalizing on four different oxidation states of vanadium ions to form two redox couples, VRBs are capable of converting electrical energy to chemical energy and subsequently releasing it in a controlled fashion when needed. Unlike traditional solid-state rechargeable batteries, VRBs store energy in the electrolyte contained in external tanks, while the energy conversion takes place in electrode compartments. As a result, the energy capacity and

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power capability of a VRB can be varied independently by adjusting the stack size and electrolyte volume accordingly for different power and energy storage applications. Due to its unique mechanism and compelling characteristics such as quick response and long cycle life, among others, VRB technology has sparked considerable research interest in developing electrochemical energy storage technologies for various grid applications such as load-leveling/peak shaving, emergency power backup, and renewable energy integration [9].

The ion exchange membrane (IEM) is one of the most important components in a RFB system; it prevents the crossover of the active materials in the positive and negative electrolytes while supporting proton transport to complete the circuit. Perfluorinated polymer membranes (e.g., NAFION® membranes) have become the choice of IEMs for VRBs due to their high conductivity and excellent chemical stability in highly oxidizing positive electrolytes [10,11]. However, even with perfluorinated membranes such as NAFION 117 [12], NAFION 212 [13], and GORE-SELECT® membranes [14], several groups have reported severe capacity decay of VRBs during cycling. Although the capacity fading mechanism is not entirely understood by the VRB research community, the inevitable crossover of vanadium ions across the membrane may play a significant role in causing the capacity fading during cycling [15]. More seriously, precipitation may occur if the vanadium ion concentration in positive electrolytes continues to increase as a result of the net transfer of vanadium ions [16]. Therefore, it is of great importance to investigate the transport behaviors of vanadium ions across the membrane, which may also shed light on the VRB capacity fading mechanism. The reactions between transported vanadium ions and native vanadium ions, however, make this study very challenging. Previous literature reports either focused on the *ex-situ* static dialysis test or the long term accumulated effect of the vanadium ion transport [15,17,18]. Without the presence of an electric field, the *ex-situ* static dialysis test cannot possibly reveal the complete transport phenomenon of the vanadium ions in real VRB operation. On the other hand, detailed vanadium ion transport information at different states of charge (SOCs) cannot be obtained from the long-term investigation.

In this paper, redox flow batteries with vanadium and iron redox couples were constructed to investigate the transport behaviors of vanadium ions. A $\text{VO}^{2+}/\text{VO}_2^+ \parallel \text{Fe}^{3+}/\text{Fe}^{2+}$ redox flow battery with $\text{VO}^{2+}/\text{VO}_2^+$ couples and $\text{Fe}^{3+}/\text{Fe}^{2+}$ couples as positive and negative active species was employed to study the transport of $\text{VO}^{2+}/\text{VO}_2^+$. Similarly, the transport of $\text{V}^{3+}/\text{V}^{2+}$ was investigated by using a $\text{Fe}^{2+}/\text{Fe}^{3+} \parallel \text{V}^{3+}/\text{V}^{2+}$ redox flow battery with $\text{Fe}^{3+}/\text{Fe}^{2+}$ couples and $\text{V}^{3+}/\text{V}^{2+}$ couples as positive and negative active species. Furthermore, a new method was designed to differentiate the concentration-gradient-driven vanadium ion diffusion and electric-field-driven vanadium ion migration. A simplified Nernst–Planck equation was established to describe the vanadium ion transport behaviors in real operation of flow batteries. Diffusion coefficients and electric-migration coefficients of VO_2^+ , VO^{2+} , V^{3+} , and V^{2+} were obtained by fitting the experimental data.

2. Experimental

Devices used in these tests included in-house designed single cells, peristaltic pumps (Cole Parmer, Masterflex® L/S® 7551), Pyrex® glass beakers as electrolyte reservoirs, and Viton® tubing. Graphite felts (GFD 5, SGL Carbon Group, Germany) with apparent area of 10 cm² were used as electrodes and NAFION® 115 as membranes in all single cells. Original electrolytes used in these tests included trivalent vanadium electrolyte (1 mol L⁻¹ V^{3+} in 5 mol L⁻¹ total Cl⁻), tetravalent vanadium electrolyte (1 mol L⁻¹ VO^{2+} in 5 mol L⁻¹ total Cl⁻), trivalent iron electrolyte (1 mol L⁻¹

Fe^{3+} in 5 mol L⁻¹ total Cl⁻), and bivalent iron electrolyte, (1 mol L⁻¹ Fe^{2+} in 5 mol L⁻¹ total Cl⁻). Trivalent vanadium electrolyte, trivalent iron electrolyte and bivalent iron electrolyte were prepared by dissolving VCl_3 (Sigma–Aldrich, 97%), FeCl_2 (Sigma–Aldrich, 98%), and FeCl_3 (Sigma–Aldrich, 98%) in concentrated HCl (Sigma–Aldrich, 37%) at room temperature. Tetravalent vanadium electrolyte was made by electrochemically charging the trivalent vanadium electrolyte. During the operation of flow batteries, electrolytes inside the reservoirs were circulated in two separate loops through the electrode compartments at a flow rate of 20 mL min⁻¹. The reservoir with trivalent vanadium electrolyte was bubbled with nitrogen for 10 min and sealed before testing to prevent V^{2+} from being oxidized to V^{3+} . A potentiostat/galvanostat (Arbin Inst., College Station, TX) was employed to carry out the charge–discharge process. Inductively coupled plasma (ICP, Optima 7300DV, Perkin Elmer), was used to measure the total concentration of vanadium ions, including VO^{2+} , VO_2^+ , V^{3+} , and V^{2+} , in each sample.

Fig. 1 is the schematic diagram of flow batteries for measuring the vanadium ion transport in real charge–discharge operation. In the $\text{VO}^{2+}/\text{VO}_2^+ \parallel \text{Fe}^{3+}/\text{Fe}^{2+}$ flow battery (Fig. 1(a)), 50 mL tetravalent vanadium electrolyte and 50 mL trivalent iron electrolyte were used as original positive and negative electrolytes, respectively. The battery was charged to 90% SOC and then discharged to 10% SOC. At each interval of 10% SOC change, a 1 mL sample was withdrawn from the negative electrolyte after the potentiostat/galvanostat program and the pump were paused. In order to minimize the change of negative electrolyte composition and volume, 1 mL pre-prepared $\text{Fe}^{2+}/\text{Fe}^{3+}$ mixed solution with calculated negative electrolyte composition at each SOC was added back to the electrolyte reservoir. The withdrawn samples were subjected to ICP analysis to determine the total vanadium ion concentration. The same procedure was applied to the $\text{Fe}^{2+}/\text{Fe}^{3+} \parallel \text{V}^{3+}/\text{V}^{2+}$ flow battery shown in Fig. 1(b). In this case, the original positive and negative electrolytes were 50 mL bivalent iron electrolyte and 50 mL trivalent vanadium electrolyte, and the samples were withdrawn from the positive electrolytes instead of the negative electrolytes.

A flow battery's configuration, as illustrated in Fig. 1(c), was designed to measure the vanadium ion diffusion driven only by concentration gradient. 50 mL tetravalent vanadium electrolyte, 50 mL trivalent vanadium electrolyte, 50 mL bivalent iron electrolyte and 50 mL trivalent iron electrolyte were used as the original electrolytes in reservoirs marked with VO^{2+} , V^{3+} , Fe^{2+} , and Fe^{3+} , respectively. Cell 1 and Cell 2 were used as diffusion cells to implement the concentration-gradient-driven vanadium ion diffusion. The SOC changes of all electrolytes were achieved by applying the current to Cell 3 and Cell 4. The procedure for this test was similar to that in the above two tests: electrolytes were charged to 90% SOC and discharged to 10% SOC, and samples were withdrawn from reservoirs marked with Fe^{2+} and Fe^{3+} at each interval of 10% SOC change. Due to the short test time, the changes of total vanadium ion concentration in vanadium-based electrolytes and of total iron ion concentration in iron-based electrolytes were neglected. Vanadium ion transport in this test was the same as that in the above two tests except that there was no electric field across diffusion cells 1 and 2. Vanadium ions transported in iron electrolytes only came from the concentration gradient between the vanadium-based electrolytes and iron-based electrolytes.

3. Results and discussion

The test results of vanadium ion transport in a $\text{VO}^{2+}/\text{VO}_2^+ \parallel \text{Fe}^{3+}/\text{Fe}^{2+}$ flow battery are shown in Fig. 2. At the current density of 25 mA cm⁻², vanadium ion concentration in negative iron-based electrolytes increased in both the charge and discharge processes,

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