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Measuring the state of charge of the electrolyte solution in a vanadium redox flow battery using a four-pole cell device



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HIGHLIGHTS

- The four-pole cell device is proposed to measure electrolyte imbalance in a VRB.
- The method is sufficiently precise to be applied in real-time mode.
- The effect of free ions in electrolyte solution on the cell voltage is discussed.
- The effect of electrolyte compositions on the performance of VRB system is described.

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ABSTRACT

The decrease in the efficiency and capacity of a vanadium redox flow battery (VRB) caused by an electrolyte imbalance is an important impediment to its long-term operation. Knowing the state of charge (SOC) of an electrolyte solution can quantify the level of the electrolyte imbalance in the VRB. In this study, a four-pole cell device is devised and employed to predict the SOC. The proposed method directly measures the ionic resistance of the electrolyte solution and is sufficiently precise to be applied in real-time mode. Experimental studies on the effects of the operating current on the four-pole cell and the concentrations of vanadium and sulfuric acid in the electrolyte solution are carried out. The results show that the four-pole cell method can be utilized to measure the electrolyte SOC. The concentrations of vanadium and sulfuric acid in the electrolyte solution affect the ionic resistance of the solution. Regarding the capacity and efficiency of the VRB system, the results indicate that the electrical charge is determined from the concentration of vanadium and that the cell voltage depends on the concentration of sulfuric acid in the electrolyte solution. The decreased vanadium concentration and increased sulfuric acid concentration improves the cell voltage efficiency.

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1. Introduction

A vanadium redox flow battery (VRB) is an energy storage technology that is based on the electrochemical principle by which electrical energy can be stored as a form of chemical energy and then re-generated when the electricity is demanded [1–3]. The key advantage of the VRB is that its power and energy can be designed separately [4–6], leading to flexibility in scale up. Furthermore, the empty energy of the electrolyte solution can be replaced by the full energy of the electrolyte solution, which is a simple way to charge the VRB system [7,8]. Consequently, the VRB system has received much attention and is found in many applications. At present, the

VRB is used together with renewable energy systems to compensate for the intermittence of the energy supply [9–11].

The VRB consists of two key components, an electrochemical cell (for energy conversion) and an electrolyte solution (for energy storage). When the VRB system needs to be used for energy storage or generation, an electrolyte solution is fed into the electrochemical cell and then the redox reaction (reduction and oxidation reactions) of vanadium occurs in the cell. The cell has two half-cells (positive and negative) that are separated by an ion exchange membrane, which is utilized to prevent cross mixing of the electrolyte between the half-cells [12–14]; however, ions can be transported across the membrane to balance the circuit during the charging or discharging process. Because vanadium is a transition element and has four oxidation states, it can be employed as both positive and negative electrolytes [15–17].

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An electrolyte solution imbalance is considered a major problem of the VRB [18–20] that is caused by side reactions and vanadium ion and water transfers across the membrane [21–23]. This problem affects the energy capacity and efficiency of the VRB system. Research groups have attempted to solve the problem through several approaches; for example, new membranes were synthesized to minimize the transfer of vanadium ions and waters across the membranes [24–27], the operation of the VRB was optimized [28–31] and the electrochemical cell and electrolyte tank were designed to decrease the side reactions [32]. Alternatively, the concept of electrolyte system management is proposed to maintain the level of the electrolyte imbalance in an acceptable range. For this approach, the determination of the state of charge (SOC) on each side of the VRB electrolyte is necessary. When the real-time measurement of the SOC can be performed, the electrolyte in the VRB system can be automatically carried out, leading to high system effectiveness.

In general, an open circuit voltage cell (OCV cell) is applied to the measurement of the total system SOC, indicating the amount of energy remaining in the VRB system. As the SOC on each side cannot be identified by this method, the level of the electrolyte imbalance cannot be determined. To detect the SOC on each electrolyte side, a potentiometric titration method with potassium permanganate as the titrant is the most popular method [18]; however, this method requires time and is thus, unsuitable for real-time applications. The measurement of the electrolyte solution absorbance can also be utilized to measure the SOC. As vanadium is a transition element, the color of the electrolyte solution changes with the vanadium oxidation state [18]. Because the positive electrolyte is opaque due to the high concentration of vanadium, this method cannot identify the SOC on the positive side. The transmission spectrum can also be utilized to determine the SOC based on the shape of the spectrum from many wavelengths instead of the absorbance at a single wavelength [20]. Although this method can be employed to detect the SOC in both the positive and negative electrolyte solutions, a large database of the standard spectra is needed for comparison with the sample spectrum. The measurement of the conductivity of the electrolyte solution is another potential method [18], but the calibration of the probe is necessary to make a precise measurement. Additionally, inserting a reference electrode is another way of knowing the state of charge at each separate electrode [33,34]. However, the reference electrode should be employed in additional cell in order to avoid the operating cell disturbance and the measurement of SOC should be done in the condition of no current flow.

In this study, the measurement of the SOC in the electrolyte on each side of the VRB using a newly developed four-pole cell with simplicity and versatility is investigated. The two outer poles are used to pass a constant current into the electrolyte, and the two inner poles are used to measure the potential difference. Based on this approach, the polarization effect is eliminated, and the voltage of the four-pole cell represents the actual voltage that results from the characteristics of the electrolyte solution [35]. The effects of key operating parameters, such as the constant current passed through the four-pole cell and the concentrations of vanadium and sulfuric acid in the electrolyte solution on the capacity and efficiency of the VRB system, are investigated.

2. Experimental

The experiment is divided into two parts, (1) measurement of the SOC in the electrolyte solution on each side of the VRB using a four-pole cell and (2) investigation of the effects of the electrolyte compositions on the capacity and performance of the VRB system.

2.1. Measurement of the SOC in the electrolyte solution on each side of the VRB system by a four-pole cell

2.1.1. Preparation of electrolyte solution

Vanadium pentoxide (V_2O_5) powder was dissolved in sulfuric acid solutions of varying concentrations. Then, an electrolysis cell was employed to adjust the oxidation state of vanadium to +3.5 (50% V(III) ions and 50% V(IV) ions) [36].

2.1.2. The four-pole cell

The four-pole cell is the device that was utilized to measure the voltage difference across the electrolyte solution when a constant current was applied. There are four poles (or electrodes) with different distances between them, as shown in Fig. 1. The poles were fabricated of conductive carbon with a thickness of 2.5 mm and a width of 7 mm. The four-pole cell was connected at the inlet of the electrolyte solution before passing through the VRB cell. After that, a power supply was employed to supply a constant current at the two outer poles. A multi-meter was utilized to measure the voltage difference between the two inner poles.

2.1.3. Experimental method

The VRB system with the four-pole cell was set up as shown in Fig. 1. Then, 230 mL of an electrolyte solution was added to each side of the cell using the pumps. A VRB cell with an effective area of 120 cm^2 was used to change the SOC through a charging process with a constant current of 80 mA cm^{-2} . Meanwhile, the OCV, the voltage of the cell and the voltage of the four-pole cell were recorded every 3 s using a Wisco data logger (model DL2200) until the OCV was unchanged, indicating that it was fully charged. Then, the same method was utilized to test the electrolyte solution on the other side.

Three variables, including the constant current through the four-pole cell and the concentrations of vanadium and sulfuric acid in the electrolyte solution, were investigated. The operating temperature, the test conditions and the parameters of the test device such as the flow rate of the electrolyte solution, the VRB cell, the constant current to charge for the change of the SOC, and the four-pole cell device were the controlled variables. To investigate the effects of the three variables on the four-pole cell operation, constant currents of 10 mA, 30 mA and 50 mA were employed through the four-pole cell. Vanadium concentrations of 1.0 mol L^{-1} , 1.5 mol L^{-1} and 2.0 mol L^{-1} with a sulfuric acid concentration of 4.0 mol L^{-1} and sulfuric acid concentrations of 3 mol L^{-1} , 4 mol L^{-1} and 5 mol L^{-1} with a vanadium concentration of 1.5 mol L^{-1} were also tested. The concentrations were selected based on the parameters of practical electrolyte solutions to verify that the four-pole cell method is applicable to real systems. The calculated charging time and OCV were utilized to represent the SOC.

In the electrolyte solution, the major components are vanadium salt and sulfuric acid, which comprise vanadium, bisulfate and sulfate ions and protons. These ions can affect the performance of the VRB system, so the effect of the electrolyte composition on the capacity and efficiency of the VRB system is also studied. It is noted that the variations in pH occurring during operation, e.g. water evaluation or hydrogen evolution, would affect the measured OCV. Hydrogen evolution at the negative electrode can lower the proton activity and lead to the precipitation of vanadium species.

2.2. Effect of electrolyte composition on the capacity and efficiency of the VRB system

The VRB system without the four-pole cell was set up as shown in Fig. 1. A single cell with an effective area of 120 cm^2 was utilized. GFD 4.6 felts (SGL) with thermal activation were employed as the fiber electrodes. An APS-4 Selemon membrane was used. Then, the

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