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Effects of operating temperature on the performance of vanadium redox flow batteries

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HIGHLIGHTS

- The effect of the operating temperature on the VRFB's performance is studied.
- The voltage efficiency and peak power density increases with temperature.
- High temperatures aggravate the coulombic efficiency drop and the capacity decay.
- The outcomes suggest that thermal management of operating VRFBs is essential.

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ABSTRACT

For an operating flow battery system, how the battery's performance varies with ambient temperatures is of practical interest. To gain an understanding of the general thermal behavior of vanadium redox flow batteries (VRFBs), we devised and tested a laboratory-scale single VRFB by varying the operating temperature. The voltage efficiency of the VRFB is found to increase from 86.5% to 90.5% at 40 mA/cm^2 when the operating temperature is increased from 15 °C to 55 °C. The peak discharge power density is also observed to increase from 259.5 mW/cm^2 to 349.8 mW/cm^2 at the same temperature increment. The temperature increase, however, leads to a slight decrease in the coulombic efficiency from 96.2% to 93.7% at the same temperature increments. In addition, the capacity degradation rate is found to be higher at higher temperatures.

1. Introduction

As the demand for clean and renewable energy sources increases, energy storage system has become a key technology, facilitating more widespread use of intermittent power generated from renewable sources such as solar cells and wind turbines. Flow batteries are promising electrochemical energy storage technologies due to several unique advantages, most significant of which are long life cycles and expandable features [1–8]. Within the realm of flow battery systems, the vanadium redox flow battery (VRFB) attracts the most attention due to its ability to avoid permanent cross contamination and bear deep charge and discharge.

VRFBs have been extensively investigated over the past decade because of the above-mentioned advantages. However, an important but rarely considered aspect for the design of this type of battery is how ambient temperatures affect the battery's performance. In real-world applications, the significant variations in ambient temperatures with places and seasons will certainly affect the battery's design, and subsequently, its rated power and capacity. Hence, a characterization of the battery's thermal parameters is essential in enhancing the efficiency and reliability of the flow battery operation. The effects of ambient temperatures on the overall battery system can be assessed by studying the effect of the operating temperature on a single cell. The operating temperature not only affects the chemical and physical properties of the electrolytes, but also influences the electrochemical process in the stack. During the electrochemical charge and discharge processes, both electrode kinetics and transport properties correlate intimately with the operating temperature. In addition, the side reaction rates involving hydrogen and oxygen evolution and vanadium crossover also depend on the operating temperature. Therefore, maximizing battery performance depends critically on the combination of these factors.

Previous studies with regard to thermal effects on VRFBs have been focused on the issue of precipitation in electrolytes, which is related not only to capacity degradation but also to pump operation reliability. Skyllas-Kazacos [9] reported that the positive electrolyte with a V(V) ion concentration larger than 2.0 M would

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precipitate over the period of a few days when the temperature was over 40 °C. Vijayakumar et al. [10,11] found that the formation of V_2O_5 caused the precipitation phenomenon in V(V) solutions. More recently, Zhang et al. [12] reported that V(IV) solution additionally suffered from precipitation at temperatures lower than −5 °C, with a concentration of 2.0 M VO^{2+}/5.0 M SO_4^{2-}; this phenomenon was attributed to a decrease in $VOSO_4$ solubility at lower temperatures. Based on the results derived from the literature, the operating temperature was restricted within the range of 10–40 °C to avoid the problem of precipitation [9–13]. To address the issue of precipitation, efforts have been made toward the stabilization of electrolytes by including a stabilizer or alternating the supporting electrolyte compositions. It has been reported that the addition of polyacrylic acid and its mixture with methanesulfonic acid can markedly improve electrolyte stability [12]. Li et al. [14] also reported that by adopting sulfate–chloride mixed electrolytes, with a vanadium content of up to 2.5 M, the electrolyte is observed to be stable within a wider temperature range of −5 to 50 °C.

A few investigations of the effects of the operating temperature on the performance of VRFBs have been reported. Kazacos and Skyllas-Kazacos [15] studied the charge–discharge performance at 30 mA/cm^2 of a VRFB that used a carbon plastic electrode at different temperatures in a range of 23–45 °C; their results showed a decrease in the coulombic efficiency (from 97% to 93%), but a slight increase of voltage efficiency (from 88% to 90%) when the temperature increased. Recently, Mohamed et al. [16] investigated the charge–discharge performance in the temperature range of 288–308 K at a constant current density of 60 mA/cm^2 and tested the discharge cell voltage at different current densities. Their result depicted that the increasing temperature reduces the overall polarization losses. However, there is still a lack of comprehensive understanding on such behaviors. In addition, building up a guidance and reference to the future mathematical modeling work on the thermal behavior of VRFBs requires more experimental data, including the efficiencies at wider temperature range, and the capacity change during long term operation.

Based on the above requirements, the objective of this work is to investigate the effects of the operating temperature on the performance of a typical VFRB system. We designed a single cell setup in which the operating temperature can be varied and controlled precisely even down to a value lower than the room temperature. The charge–discharge behavior, discharge polarization curves, and capacity degradation with cycles were measured. In addition, cyclic voltammetry experiments were conducted to study the reaction kinetics of both V(II)/V(III) and V(V)/V(IV) redox couples. Furthermore, viscosity measurements were conducted to investigate changes in pump work consumption.

2. Experimental methods

2.1. VRFB single cell

A battery test system (Arbin Instruments) was used to conduct the charge–discharge, polarization curves and internal resistance tests. The architecture of the flow battery was similar to that of Leung et al.'s design [17] with an electrode area of 5 cm^2, and a pair of aluminum homemade cooling plates installed against the current collectors, which is used to control the operating temperature. Fig. 1a depicts the single cell, consisting of two acrylic flow channels (5 mm thickness), four silica gaskets (1.5 mm thickness) and two graphite felt electrodes (6 mm thickness, Sigratherm® GFA-05, SGL Carbon, Germany). An ion-exchange membrane (Nafion 115) was used to separate the electrodes. Electrolytes were fed into the compartments of the acrylic flow channels and circulated to and from the tanks with a flow rate of 50 ml/min. Water from a bath kept at a constant temperature was pumped into the cooling plates, while a thermocouple was installed in the fixture to monitor and regulate the operating temperature as shown in Fig. 1b.

The electrolyte at the positive side was prepared by dissolving 1.0 M vanadyl sulfate powder (ZhongTian Chemical Ltd. China) in a 4.0 M sulfuric acid solution. Meanwhile, the electrolyte at the negative side was initially prepared with an identical solution, and electrochemically reduced to trivalent state by an electrolytic cell.

In the charge–discharge and cycling experiments, the volume of the electrolyte at both the positive and negatives sides was 20 ml. The polarization curve test adopted an electrolyte at a volume of 25 ml for both sides. In the polarization curve test, the State of Charge (SOC) at the starting point was about 90% and was reduced to 69% by the end of the experiment.

2.2. Cyclic voltammetry

The cyclic voltammetry experiment was conducted in a three-electrode system to investigate the electrochemical behavior of both V(III)/V(II) and V(V)/V(IV) redox couples. The working

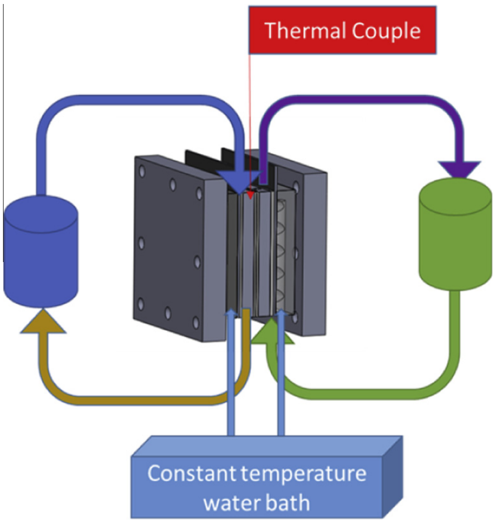

Fig. 1b. Single cell with an operating temperature regulation system.

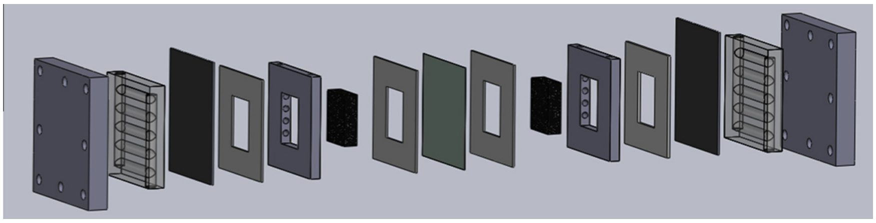

Fig. 1a. Single cell with home-made cooling plates.