

Parametric study and flow rate optimization of all-vanadium redox flow batteries



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HIGHLIGHTS

- Performance and efficiency of all-vanadium redox flow batteries were studied.
- Relationship between ion concentration and parameters in the system was analyzed.
- Steady state and transient responses established an optimal operating strategy.
- An empirical equation is suggested to maximize the energy efficiency of the systems.

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ABSTRACT

The parametric study for an all-vanadium redox flow battery system was examined to determine the optimal operating strategy. As dimensionless parameters, the stoichiometric number and state of charge were used to apply the strategy to all scales of the flow battery system. In this study, we developed a transient model for this system, which is supported by experimental data, to analyze effect of parameters on the ion concentration and determine its optimal operating conditions. First, the performance of the flow battery system was analyzed in steady-state conditions to examine the changes of the ion concentration depending on different flow rates, current densities, and sizes of active area. As flow rate increases, the energy efficiency slightly increases, because faster flow rates can deliver more vanadium ions from the reservoir. The energy efficiency decreases according to current density, because large current results in large amount of ohmic loss of membrane. When the size of active area increases, the energy efficiencies remain constant, however, the cycle time decreases. Next, the transient response for the system was analyzed by changing the stoichiometric number and current density during the charge and discharge processes. Variation of the system's energy efficiency was studied with changes in the stoichiometric number and state of charge as the current density was varied from 20 to 100 mA/cm². Increasing the flow rate at the beginning of the charge–discharge process is more efficient in the low current density region. At a current density of 100 mA/cm², however, it is better to increase the flow rate after the state of charge reaches 50%. Lastly, an operating strategy is suggested that involves controlling the mass flow rate of the electrolyte during the charge–discharge process. The operating strategy is presented as an empirical equation defined by the stoichiometric number and state of charge. Notably, this equation can contribute to improving the performance of all scales of the flow battery system by simply changing the electrolyte flow rate at right time.

1. Introduction

Large-scale energy storage systems (ESSs) are a promising solution to ease the problems associated with intermittent power delivered from renewable energy sources such as wind and solar energy. All-vanadium redox flow batteries (VFBs) have received considerable attention as a

candidate for large-scale ESSs due to their long cycle life, flexibility for scale-up, quick response, and low maintenance cost [1,2]. However, many performance challenges of VFBs required by the market persist; low ion selectivity of the membrane, low energy density, and a lack of studies on its optimization have limited further commercialization of this type of flow battery [3].

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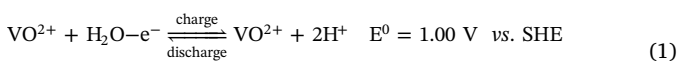
Many researchers have attempted to improve the performance of VFBs by developing materials. Some researchers tested high voltage redox pairs of vanadium/vanadyl acetylacetonates and Zn/Ce as an electroactive material to develop safe and high voltage aqueous redox flow battery system [4]. Other researchers tried to increase operating current density through KOH-activated carbon electrode [5,6]. Others developed dense polybenzimidazole membranes that has highly proton conductive and low vanadium permeability to increase energy efficiency [7]. On the other hand, there are researches to improve performance of the VFB system by distributing the electrolyte uniformly in the electrode. Some studies compared the flow field for flow-through channel and flow-by channel [8,9], and other studies investigated flow field in various designs of flow channel [10]. Others explained the importance of the compression force for mass transport of the electrolytes [11]. Others analyzed variation of ion concentration by considering mobility of ions [12] and develop an estimator to monitor capacity loss [13,14]. Unfortunately, relatively few studies have examined the effect of operating conditions on the performance of VFB systems.

Few studies have been conducted to improve performance by changing operating conditions. Some studies tried to reduce capacity fade by altering charging and discharging currents [15]. Other studies have attempted to maintain the operating temperature to prevent thermal precipitation in the cell by controlling the flow rate [16,17]. Others suggested operating strategies to increase the performance of VFB systems by changing the electrolyte flow rate [18]. Although a few studies have reported the effect of operating condition on the performance of VFBs, the lack of quantitative and transient analysis makes it difficult to utilize previous results to develop an optimal operating strategy for individual systems. Moreover, the present data remain insufficient to explain the relationship between the ion concentration and operating parameters in transient state.

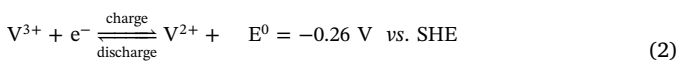
In this study, we analyze the steady-state and transient responses of a VFB system and suggest an optimal operating strategy to maximize its performance for various current density by controlling the flow rate during the charge–discharge process. The discussion begins with an explanation of the steady-state results with experimental and numerical analyses to understand the changes of the ion concentration depending on different mass flow rates, current densities, and sizes of active area. Next, the effect of changing the flow rate and current density on the ion concentration change during the charge and discharge processes is investigated in order to observe the transient behavior of the VFB system. Then, the effect of the flow rate change under various states of charge is studied to understand the relationship involving the flow rate, state of charge, and current density. Lastly, the obtained results are considered in the development of operating strategies for maximizing the energy efficiency of VFB systems.

2. Methodology

A VFB system is mainly composed of a pump, reservoir, and stack, as shown in Fig. 1. Electrolytes are stored in each reservoir and pumped into the cells, which determines the battery's power via electrochemical reactions; $V^{2+}/3+$ and $V^{4+}/5+$ solutions are stored in the reservoirs and circulated in the negative and positive sides, respectively. The standard voltage of the VFB is 1.25 V, which is produced by reactions at the anode and cathode. At the positive electrode:



At the negative electrode:



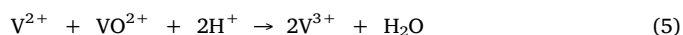
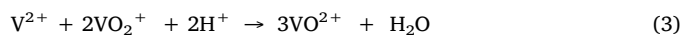
In this study, a model for VFB is developed and experimentally validated to analyze the steady and transient responses. We calculated

the concentrations of each species at the electrodes and reservoir to obtain the performance of the VFB system. To consider transient mass transport phenomena within the VFB system, the mass transport of species, electrochemical reactions during the charge–discharge process are also included. Additionally, power consumption of pump is calculated to evaluate VFB system performance. The flow chart for VFB system model is presented in Fig. 2. Furthermore, the experimental setup was prepared to substantiate the developed model and determine an optimal operating strategy.

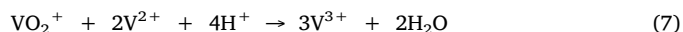
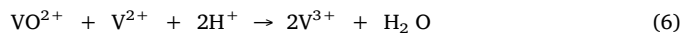
2.1. Modeling

We developed a VFB system model to examine the steady and transient responses with reference to previous studies. The stack and reservoir model is developed in quasi one-dimensional dimensional to analyze variation of state of charge (SOC) between inlet and outlet. An isothermal condition is assumed in the entire system. Furthermore, crossover of vanadium ions and water molecules are considered, and possible side reactions are considered, as well.

First, the concentrations of vanadium ions at each electrode were quantified using mass conservation equations [19]. Self-discharge reactions across the membrane due to concentration gradients were also considered to explain the effect of the operating parameters on the VFB efficiency [20]. At the positive electrode, V^{2+} and V^{3+} ions diffuse from the negative side and react with ions in the catholyte:



At the negative electrode, reactions occur in the anolyte with VO_2^+ and VO_2^+ ions that diffuse from the positive electrode:



Since the products of side reactions (5) and (8) can react repeatedly with VO_2^+ and V^{2+} in reactions (4) and (6), we have neglected V^{3+} and VO^{2+} generated from those reactions in our model [20]. Here, we assumed that the ions are circulated between the reservoir and stack by convection and are transported through the membrane by diffusion [21]. Based on the above explanation, concentration changes of V^{2+} and V^{3+} at the negative electrode during charge can be expressed as follows:

$$\begin{aligned} \varepsilon V_e \frac{dC_{V(II)}}{dt} = & Q(C_{V(II)}^{res} - C_{V(II)}) + A_s \frac{j}{F} - \frac{A_m}{t_m} (D_2 C_{V(II)} + 2D_5 C_{V(V)} \\ & + D_4 C_{V(IV)}) \end{aligned} \quad (9)$$

$$\begin{aligned} \varepsilon V_e \frac{dC_{V(III)}}{dt} = & Q(C_{V(III)}^{res} - C_{V(III)}) - A_s \frac{j}{F} - \frac{A_m}{t_m} (D_3 C_{V(III)} - 3D_5 C_{V(V)} \\ & - 2D_4 C_{V(IV)}) \end{aligned} \quad (10)$$

Here, ε is porosity; V_e is the electrolyte volume; C_i^{res} and C_i are the concentrations of the vanadium species at the reservoir and the VFB cell, respectively; Q is the flow rate; j is the current density; A_s is the active surface area for the reaction, which is written as SV_e , where S is the specific surface area for the reaction and is used as a fitted parameter; A_m is the membrane area; t_m is the membrane thickness; and D_i is the diffusion coefficient for each species, which is listed in Table 1. Concentration changes at the positive side during charge can be expressed as:

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