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Modeling the effect of shunt current on the charge transfer efficiency of an all-vanadium redox flow battery

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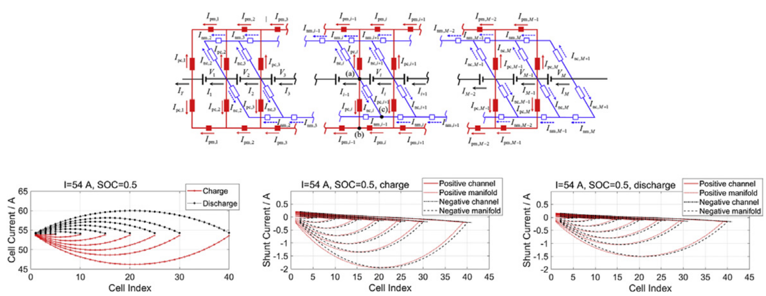
HIGHLIGHTS

- A shunt current model and a solution method are presented in detail.
- The maximum shunt current is located in the central manifold of a VRFB stack.
- Shunt-current loss is higher at the conditions where the cell voltage is higher.
- The charge-transfer efficiency is analyzed for various battery design parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

In an all-vanadium redox flow battery (VRFB), a shunt current is inevitable owing to the electrically conductive electrolyte that fills the flow channels and manifolds connecting cells. The shunt current decreases the performance of a VRFB stack as well as the energy conversion efficiency of a VRFB system. To understand the shunt-current loss in a VRFB stack with various designs and operating conditions, a mathematical model is developed to investigate the effects of the shunt current on battery performance. The model is calibrated with experimental data under the same operating conditions. The effects of the battery design, including the number of cells, state of charge (SOC), operating current, and equivalent resistance of the electrolytes in the flow channels and manifolds, on the shunt current are analyzed and discussed. The charge-transfer efficiency is calculated to investigate the effects of the battery design parameters on the shunt current. When the cell number is increased from 5 to 40, the charge transfer efficiency is decreased from 0.99 to a range between 0.76 and 0.88, depending on operating current density. The charge transfer efficiency can be maintained at higher than 0.9 by limiting the cell number to less than 20.

1. Introduction

All-vanadium redox flow batteries (VRFBs) are considered one of the most promising candidates for load leveling and peak shaving for renewable energy sources, including solar and wind power [1–3], owing to their long life, low self-discharge, and flexible design. Their energy capacity depends on the electrolyte volume, whereas their power output depends on the stack size. The stack comprises several single cells to meet the voltage requirement. Each single cell is separated by bipolar plates, in which flow channels are designed to distribute electrolytes. Owing to the conductivity of the electrolyte, a shunt current arises in the manifolds connecting cells and the flow

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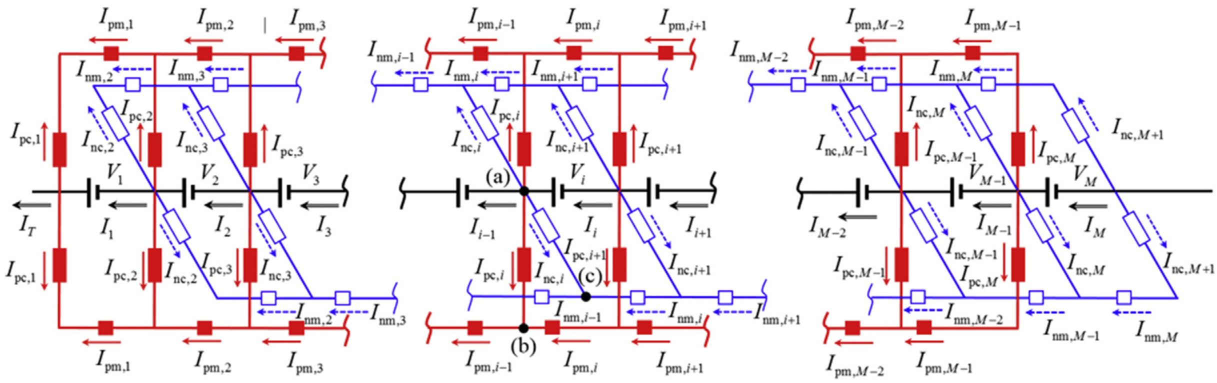

Fig. 1. Equivalent electrical circuit of the shunt currents in a VRFB stack.

channels connecting the manifold and the active area when a VRFB operates. The presence of shunt current causes capacity loss, resulting in a decrease in the energy conversion efficiency. Thus, understanding the effects of the shunt current on the battery performance and minimization of the shunt current are important issues in the development of a VRFB stack.

Most currently published works have focused on the key components of VRFBs, such as porous electrodes [4,5], separators [6], and bipolar plates [7,8]. However, only a few works report on the shunt current of the VRFB. Xing et al. [9] developed a shunt-current model for a VRFB stack based on the electrical circuit analog method. The distributions of the shunt currents in the flow channels and manifolds on the positive and negative sides were presented in detail. They suggested that a reduction in the number of cells, a decrease in the resistances of the manifolds and channels, and an increase in the power of a single cell helped to reduce the shunt-current loss. Tang et al. [10] combined a shunt-current model and thermal model to investigate the effects of shunt current on stack efficiency and the variation in the temperature of the stack with 40 cells under standby conditions. Their model predicted that shunt current significantly contributed to the increase in the stack temperature.

The direct measurement of shunt currents within a VRFB stack is a challenging task because the manifolds and flow channels are enclosed within the stack. Fink et al. [11] used a five-cell miniature VRFB stack with an external hydraulic system to directly measure the shunt current. They also developed a shunt-current model to study the effects of shunt current on coulombic efficiency. Experimental results showed that the inner cells of a stack discharge faster than the outer cells. Yin et al. [12] developed a coupled three-dimensional electrochemical model to investigate the shunt-current distribution and its effects on coulombic efficiency. The model was validated using a five-cell short stack. The short-flow channel design in their study provided a significant shunt-current loss of approximately 23%.

The aforementioned studies suggested that shunt currents could be reduced by increasing the electrical resistance of the electrolyte circuit. Therefore, the flow channels on the frame with a longer path or smaller cross-sectional area are preferred. However, the pressure drop of the electrolyte flow increases, resulting in an increase in the power consumption of the pumps. As a result, an analysis of the trade-off between the shunt current and the pumping power is essential to achieve the maximum energy efficiency of the system in a battery design. König et al. [13] developed a Matlab/Simulink model to investigate the effects of a piping system design on the shunt currents of a multistack system. Their results showed that the shunt current increased in the piping system connected to the VRFB stacks and was affected by the pipe diameter and length as well as the number of VRFB stacks in series. Ye et al. [14] studied the effects of the piping geometry and battery design on the shunt current and pumping power consumption using an analog circuit model and flow network model. Recently, Skyllas–Kazacos et al. [15] showed that bipolar electrodes provide an internal pathway for electrons in the presence of interconnecting channels and manifolds that complete the circuit and concluded that a larger number of cells in the stack leads to a larger number of internal pathways for electrons and protons, resulting in larger shunt-current losses.

Although shunt currents in a single VRFB stack have been numerically or experimentally investigated, the study on the effect of operating conditions, such as SOC and current during a charge or discharge process, on shunt currents has not been widely reported. In this study, a mathematical model based on an equivalent electric circuit analogy is proposed to investigate the shunt current of a VRFB stack under various operating conditions. The model is solved through a simple and quick solution process and calibrated using a 19-cell VRFB stack. The distribution of the shunt current and its effects on the stack performance are analyzed and discussed in terms of charge-transfer. Further improvements in the stack design and the operating strategy are suggested to reduce the shunt-current loss.

2. Mathematical model

2.1. Governing equations

This model was simplified with the following assumptions:

(1) The electrical potential is uniform throughout the active area.
(2) The shunt currents in the inlet and outlet channels are the same in a single cell.
(3) The temperature and electrolyte concentration within a single cell are uniform.

Both the anolyte and catholyte are conductive, causing current to flow in the manifolds between cells and the flow channels between a manifold and the active area. The shunt current within a VRFB stack can be modeled as an equivalent electrical circuit, as shown in Fig. 1. The VRFB stack comprises M cells connected in series. R_{pc}, R_{nc}, R_{pm}, and R_{nm} represent the equivalent resistances of the electrolyte within the positive channel, negative channel, positive manifold, and negative manifold, respectively. $I_{pc,i}$, $I_{nc,i}$, $I_{pm,i}$, and $I_{nm,i}$ represent the currents flowing through the positive and negative channels within the i-th cell. I_i and V_i represent the cell current and voltage generated by the i-th cell, respectively. The resistance can be determined with the known flow frame design and electrolyte conductivity; the shunt current and cell current can be determined using this model. The shunt currents in the inlet and outlet channels are the same; as a result, there are $(5M - 2)$ unknowns for an M-cell stack, and $(5M - 2)$ equations are required to