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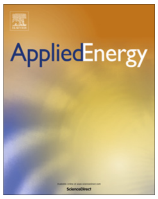

Numerical and experimental studies of stack shunt current for vanadium redox flow battery

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HIGHLIGHTS

- A coupled three-dimensional model of VRB cell stack is developed.
- Shunt current of the stack is studied with the model and experiment.
- Increased electrolyte resistance in channel and manifold lowers the shunt current.
- Shunt current loss increases with stack cell number nonlinearly.

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ABSTRACT

The stack shunt current of VRB (vanadium redox flow battery) was investigated with experiments and 3D (three-dimensional) simulations. In the proposed model, cell voltages and electrolyte conductivities were calculated based on electrochemical reaction distributions and *SOC* (state of charge) values, respectively, while coulombic loss was estimated according to shunt current and vanadium ionic crossover through membrane. Shunt current distributions and coulombic efficiency are analyzed in terms of electrolyte conductivities and stack cell numbers. The distributions of cell voltages and shunt currents calculated with proposed model are validated with single cell and short stack tests. The model can be used to optimize VRB stack manifold and channel designs to improve VRB system efficiency.

1. Introduction

Vanadium redox flow battery (VRB) system, as one of the most promising electrochemical energy storage system (EESS), is attracting more and more attention over the last decade [1–7]. Due to its advantages such as high energy efficiency, long cycle life and flexible capacity for system design, VRB can be used for load leveling, peak shaving, back-up power systems and power plant combined with renewable energy sources such as wind and solar. A number of installations of VRB systems for both demonstration and commercial application have been reported over the world [8–11].

VRB which was pioneered by Skyllas-Kazacos et al. is mainly composed of cell stacks to generate electricity, tanks to contain electrolyte solutions and liquid pumps to circulate the fluid from tanks to stacks [12,13]. Cell stack, the electrochemical reactor, is assembled by a number of single cells which are electrically connected by bipolar plates in series to achieve higher voltage. In most of the designs, positive/negative electrolyte flows from manifold to each individual cell in parallel. As all individual cells share the inlet and outlet manifolds, they are electrically connected by the electrolyte solutions for electric conductivity of the fluid. Therefore, the shunt current exists between different individual cells during the operation. The coulombic loss caused by the shunt current is one of the most important factors leading to battery's capacity loss and material's corrosion for VRB stack. To enhance the coulombic efficiency of VRB stack and system energy conversion efficiency, more fundamental work should be carried out to study the shunt current mechanisms and find out engineering design solutions to eliminate or reduce its negative effects on VRB system efficiency.

There are many fundamental researches and studies regarding VRB key materials synthesis and characterization, cell stack design and test, as well as theoretical simulations [14–31]. Only a few researches are carried out concerning stack shunt current so far, most of which are numerical simulations based on equivalent circuit model. White et al. proposed a circuit analog model to predict shunt current in stacks with undivided and divided bipolar plate

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cells [32]. Xing et al. analyzed VRB's shunt current loss and its distributions using a circuit analog method [33]. Tang et al. investigated the effect of shunt current and stack temperature on battery efficiency with electrical circuit analogy [34]. Wandschneider et al. proposed a multi-stack simulation module of shunt currents for VRB system consisting of three stacks based on an equivalent circuit [35].

In this paper, a coupled three-dimensional (3D) electrochemical model with the actual dimension of the experimental cell stack is proposed to investigate the shunt current distribution and its effect on coulombic efficiency. Corresponding experimental work with VRB single cell and 5-cell short stack are carried out to study the shunt current loss and validate the proposed model.

2. Experimental

2.1. Single cell structure

Single cell and short stack of VRB are assembled for the experiment of charge and discharge. As shown in Fig. 1, two PVC (polyvinylchloride) frames are used in a single cell to construct positive and negative electrode chambers which are divided by a Nafion 115 proton exchange membrane. The carbon felts with dimensions of 96 mm × 60 mm × 4 mm provide as porous electrodes for electrochemical reactions of vanadium ions at the two sides:

Negative electrode: $V^{3+} + e^- \rightleftharpoons V^{2+}$
Positive electrode: $VO^{2+} + H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^-$

PTFE (polytetrafluoroethylene) gaskets and rubber O-rings are applied between the adjacent cell compartments for sealing and the cell components are fastened together with two stainless steel endplates and four tie rods. The single cell components indicated in Fig. 1 are duplicated when assembling a VRB cell stack. The fluid inlets and outlets of the cell are constructed at the side of the polymer insulators with a thickness of 30 mm. Current collectors made of copper are embedded in the two polymer insulators with appropriate sealing designs to avoid direct contact with electrolyte solutions.

2.2. VRB test system

To study shunt current effect and evaluate performance of the VRB cell stack, we designed a test system which is composed of the balance of plant (BOP) subsystem, data collector, controller and electronic power source and load. As shown in Fig. 2, the BOP subsystem constructed on a double-layer stainless steel platform involves two peristaltic pumps to feed the electrolyte, two electrolyte tanks with nitrogen gas protection, and PVC pipes to circulate the electrolyte solutions. The flow rates of liquid pumps are adjustable for varied operating conditions. An electronic power source (Maynuo DC Source Meter, M8852) and load (Maynuo DC Electronic Load, M9812) are used for the charge and discharge processes. A data collecting module and a programmable controller are designed to regulate and monitor the operating parameters such as flow rate, cell voltage and applied current. The data acquisition card based on the microchip (dsPIC33EP256MU810) and high precision differential amplifiers (INA118UB) are employed for all measurements and the control software programmed on LabView platform is developed for real-time data collection.

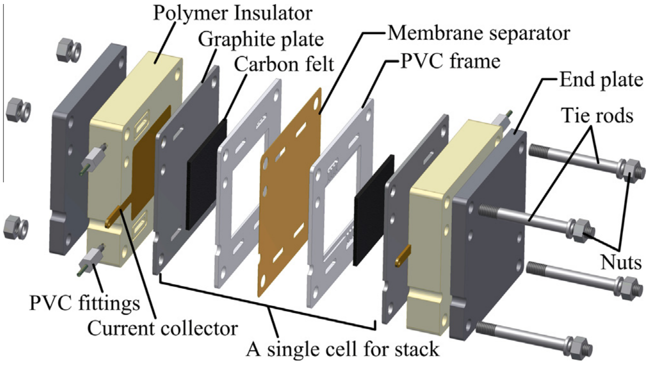

Fig. 1. Schematic of the VRB single cell assembly structure.

To conduct VRB cell stack performance evaluation, the starting electrolyte solutions for positive and negative vanadium half-cells are aqueous solution of 1.5 mol/L vanadyl sulfate $VOSO_4$ and 1.5 mol/L tri-sulfate $V_2(SO4)_3$, respectively, and 2 mol/L sulfuric acid H_2SO_4 are used for both sides. Performance of single cell and five-cell short stack during charge and discharge cycles is tested with constant flow rate of 6 ml/s and 30 ml/s respectively, at current density of 60 mA/cm^2.

3. Model development

3.1. Geometric model building

As depicted in Fig. 3, the theoretical model of VRB is based on the dimension of the experimental cell stack which is composed of graphite plate, porous electrode, membrane separator, current collector and electrolyte domains. Electrolyte solutions containing vanadium ions of different valences, V^{2+}/V^{3+} for the negative electrode and VO^{2+}/VO_2^+ for the positive electrode, are indicated with blue and green color respectively. The cross section area of manifold is 1.64 cm^2 and depth of electrolyte flow channel designed in the PVC frame is 2 mm.

3.2. Model assumptions and boundary conditions

The assumptions for the proposed model are listed below:

(1) *SOC* (state of charge) which defines vanadium ion concentrations varies with time. When the electrolyte tank is sufficiently large, the change of *SOC* is relatively small during a very short period of operation. Thus the dynamic model could be simplified as a stationary one to reduce solving time for the large geometry without losing much accuracy.
(2) The presented model is isothermal.
(3) The diluted-solution approximation is applied.
(4) The fluid flow is treated as incompressible flow.
(5) The material properties of electrode, electrolyte and membrane domains are homogeneous.
(6) Only protons could cross over through the membrane.
(7) Side reactions such as hydrogen and oxygen evolutions are neglected.
(8) Electrolyte volume change due to water permeation or water drag through membrane is ignored.

As the proposed 3D coupled model is stationary, voltages during charge and discharge processes are calculated with various inlet boundary conditions of *SOC*, which are expressed as: