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Three-dimensional, transient, nonisothermal model of all-vanadium redox flow batteries

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ABSTRACT

A three-dimensional (3-D), transient, nonisothermal model of all-vanadium redox flow batteries (VRFBs) is developed by rigorously accounting for the electrochemical reactions of four types of vanadium ions (V^{2+}, V^{3+}, VO^{2+}, and VO_2^+) and the resulting mass and heat transport processes. Particular emphasis is placed on analyzing various heat generation mechanisms, including irreversible and reversible heat generation due to vanadium redox reactions and joule heating arising from the solid electrode and electrolyte ionic resistances. The 3-D model is validated against voltage evolution curves measured under charging and discharging processes. The model predictions compare well with the experimental data over a wide range of state of charge (SOCs), and further reveal key electrochemical and transport phenomena inside VRFBs through multidimensional contours of solid electrode/electrolyte potentials, species concentrations, and temperatures. This full 3-D comprehensive VRFB model can be applied to realistic multicell stacks to determine the optimal design and operating conditions.

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1. Introduction

In recent decades, redox flow batteries (RFBs) have received considerable attention for large-scale energy storage applications. Among several RFBs classified by active species and solvents, all-vanadium RFBs (VRFBs) using different oxidation states of vanadium as negative and positive half-cell electrolytes exhibit superior characteristics such as longer life cycles, simple cell design, and minimal electrolyte cross-contamination effects [1]. To date, substantial research has been made to advance the VRFB technologies, mainly in the fields of electrodes, electrolytes, membranes, and current collectors [2–8]. In addition to the basic research at the component level, several VRFB systems on the order of kW to MW were built and successfully demonstrated in the US, Europe, Canada, Australia, Japan, and China [9–11].

VRFB technologies need to be further advanced to meet cost, performance, and durability requirements to enable their widespread use. For instance, the capital cost of VRFBs estimated in 2008 was nearly $2500/kW and is intended to be reduced to $250/kWh in 2015 and $100/kWh by 2030 [12]. Therefore, industries have focused their efforts on VRFB design and optimization for superior performance, extended durability, and cost reduction. Modeling and simulations of VRFBs are essential to obtain a comprehensive understanding of the key physicochemical and transport phenomena in VRFBs and to effectively optimize VRFB materials, component designs, and operating strategies.

In the last five years, a significant amount of effort has been devoted to the development of fundamental VRFB models. Numerical modeling and simulations of VRFBs were first introduced by Shah et al. [13]. They developed a two-dimensional (2-D) transient VRFB model, which accounted for the overall half-reactions (i.e., reduction and oxidation of vanadium species) and the resulting transport of vanadium ions, hydrogen ions (H^+), water, and sulfuric acid (i.e., HSO_4^-). However, several key phenomena such as the crossover of vanadium ions through the membrane, side reactions, thermal effects, and electron transport were neglected in their model. Later, the model was improved by incorporating the energy balance equation and various heat source terms to include both the reversible and irreversible heat generation [14]. They primarily explored the thermal responses of VRFBs under different currents, electrolyte flow rates, and external thermal boundary conditions. You et al. [15] presented a simplified version of the 2-D isothermal model of Shah et al. [13], where the transient terms in the governing equations were eliminated by pre-calculations of the Nernst potentials of the positive and negative electrodes at any given time. However, an additional voltage drop of 140 mV had to

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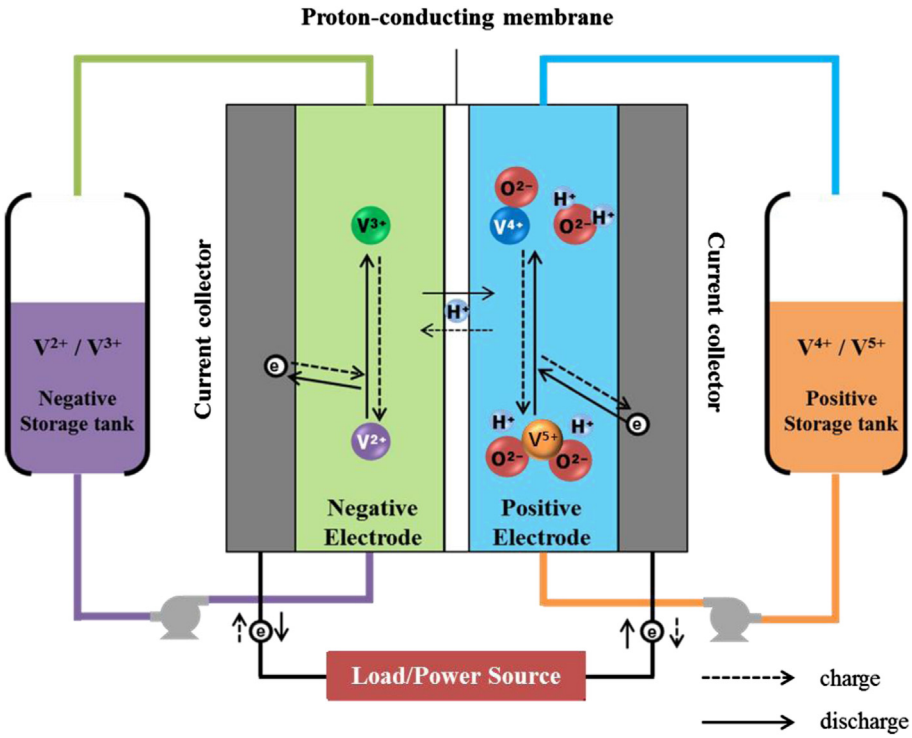

Fig. 1. Schematic diagram of VRFB with cell components and transport processes modeled in this paper.

be added to the simulation results in order to achieve reasonable agreement with the experimental data. Most recently, Knehr et al. [16] presented a 2-D, transient, isothermal VRFB model, where the species crossed over through the membrane by all the three modes (i.e., convection, diffusion, and migration) and the resulting side reactions were taken into account. They numerically predicted capacity loss due to vanadium crossover during the 45 charge/discharge cycles.

Regarding heat removal and thermal management issues, it is apparent that flow batteries have a great advantage over conventional batteries because of their built-in heat exchangers by electrolyte circulation. However, it should be noted that thermal management is still a critical factor needed to ensure high performance and durability of VRFBs. For instance, thermal precipitation of VO_2^+ in the positive electrolyte and vanadium crossover through the membrane are greatly exacerbated at higher temperatures, whereas a lower VRFB temperature (below 10 °C) can lead to the precipitation of V^{2+} in the negative electrolyte [17], implying that the temperature of VRFBs should be managed within a narrow range, i.e., ~10–40 °C [17–19]. Despite the significant thermal influence on VRFBs, previous thermal VRFB models presented in the literature were limited to a 2-D commercial fluid dynamics (CFD) model [14,17,20,21]. Some of these models were based on simple heat and mass balance equations, and did not consider the electrochemical reactions and resulting voltage losses [17,21].

In this paper, we present a rigorous 3-D electrochemical transport-thermal coupled model for VRFBs. The main focus of this study is on multidimensional thermal modeling, simulations, and a detailed analysis of VRFBs. In particular, the electrode and electrolyte potential distributions in the various VRFB components and location-specific heat source terms in VRFB models and their contributions to the overall energy balance that were not precisely studied in the literature, are addressed here under various charge/discharge cycles. Furthermore, a significant thermal gradient is expected in all three dimensions of VRFBs during charging and discharging processes. Hence, we investigate the thermal behavior of VRFBs under a 3-D VRFB geometry, showing detailed 3-D distributions of temperatures and species, and we elucidate the multidimensional thermal effects during VRFB operations.

2. Numerical model

2.1. Model assumptions

The model considers the major components of a VRFB single cell geometry that includes the membrane, porous positive/negative electrodes, and current collectors. The main assumptions of the model include the following:

1. The electrolyte flow is incompressible and laminar because of a small pressure gradient and low flow velocity.
2. Species crossover through the membrane and the resultant side reactions are neglected.
3. The evolution of hydrogen and oxygen and the accompanying gas bubble formation in the electrodes are ignored.
4. The dilute-solution approximation is used to describe species transport.
5. The ion transport mechanism driven by migration is neglected. The properties of the electrode, electrolyte, and membrane are assumed to be isotropic.

2.2. Electrochemical reactions

The main electrochemical reactions and resultant species transport in VRFBs are shown in Fig. 1. During the charge/discharge of a VRFB, the redox reactions occurring in each electrode are as follows:Negative electrode:

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