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Dynamic control strategy for the electrolyte flow rate of vanadium redox flow batteries

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HIGHLIGHTS

• A transient model of the VRB system is developed.

• The model is used for dynamic control for electrolyte flow rate of VRB.

• Flow rate is optimized under varying (dis-)charge power and SoC conditions.

• Concentration discrepancy of active species in the stack and tank is considered.

• Relatively low electrolyte flow rates are preferred with high pressure drops.

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ABSTRACT

The vanadium redox flow battery (VRB) is considered to be one of the most promising technologies for large-scale energy storage, with the electrolyte flow rate capable of significantly affecting the mass transfer, temperature rise, and pump power losses of the VRB system. Although the flow-rate optimization under constant current has been addressed in the literature, few studies have investigated the control strategy for the electrolyte flow rate under varying (dis-)charge power that is common in practical applications. Moreover, fewer studies have considered the concentration discrepancy of the active species in the tank and stack in the flow-rate optimization. In this paper, the electrolyte flow-rate optimization is investigated by incorporating the influences of the flow rate on the mass transfer, temperature rise, and required pump power. A transient model of the VRB system is developed to derive the total power losses (by which the overall system energy efficiency is determined; include losses resulting from overpotentials, ohmic drops, and required pump power) as a function of the applied current, concentration of the active species in the stack, and flow rate of the electrolyte. Based on this model, a dynamic flow-rate control strategy is proposed for determining the optimal flow rate under varying (dis-)charge power and state-of-charge conditions. The simulation results show that the proposed control strategy can deliver a high VRB system efficiency of 87.7%, and manage the electrolyte temperature to the safe range during mild summer days.

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1. Introduction

The temporal mismatch between electricity generation and consumption is becoming a leading challenge for today's energy system [1,2]. The accelerated integration of intermittent renewables (such as solar and wind) to the existing electricity grids induces considerable stress on the current generation settings [3]. As a result, the peaking and load-following generation units

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http://dx.doi.org/10.1016/j.apenergy.2017.07.065 0306-2619/© 2017 Elsevier Ltd. All rights reserved. need to run partly loaded and stay idle over much of the year [4–6]. These challenges pose a critical need for electric energy storage [1,7], which is expected to play a vital role in future energy systems by temporally decoupling electricity generation and consumption [8]. The vanadium redox flow battery (VRB) is regarded as one of the most important electric energy storage technologies with flexible energy and power configurations [9], high round-trip efficiency [10], long cycling lifetime [11], ease of scalability, and considerable potential for substantial cost reductions in the near future [12,13]. Unlike other electrochemical energy storage technologies, VRBs store energy in the redox species that are continuously circulated through the electrodes by pumps upon

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| Nomenclature | | | |
|--------------|---|----------------|---|
| VRB | vanadium redox flow battery | w | width |
| SoC | state of charge | Ζ | unit activity coefficient |
| OCV | open-circuit voltage | | |
| Α | area | Greek symbols | |
| С | mole concentration of the specific species | γ | reaction rate constant |
| Cp | specific heat capacity of the electrolyte | δ | thickness of the diffusion layer |
| D | diffusion coefficient of the specific active species | 3 | porosity of the electrode |
| d | diameter | η | overpotential of the cell |
| E | potential | $\dot{\theta}$ | pressure drop coefficient of the electrode |
| E^0 | standard potential of the overall reaction (at a pressure | κ | local mass transport coefficient of the electrolyte |
| | of 100 kPa) | λ | permeability coefficient of the electrode |
| F | Faraday constant | μ | viscosity of the electrolyte |
| fac | multiplying factor applied to the minimum flow rate | ρ | density of the electrolyte |
| H | heat exchange coefficient | σ | effective conductivity |
| h | height | | |
| I | current applied to the cell | Subscript | |
| i | applied current density per electrode surface area | act | activation |
| J | species j | amb | ambience |
| k | the kth iteration | b | bipolar plate |
| M | number of cells in a VRB stack | con | concentration |
| N | number of stacks within the VRB system | cl | cell |
| n | the nth cell in the VRB stack | d | demand |
| P | power | e | electrolyte |
| p | pressure | ed | electrode |
| Q | electrolyte flow rate (the total flow rate for all the | eq | equivalent |
| à | Statks) | lim | limit |
| Ч Р | resistance | m | membrane |
| Л D | melar rac constant | neg | negative electrode |
| Кg T | fillolal gas collisiant | pos | positive electrode |
| 1 t | at time t | S | stack |
| V | volume | surf | surface |
| v | velocity of the electrolyte | tk | tank |
| v | velocity of the electrolyte | | |

charge and discharge, while batteries, such as lithium-ion batteries, store energy within the electrode structure through charge transfer reactions, and fuel cells, which are not rechargeable, store energy in the reactants that are externally fed into the cells [1]. This feature gives VRB considerable design flexibilities but also a disadvantage of increased system complexity.

Driven by the rapid expansion of intermittent renewables [14], significant attention has been devoted to improving the energy efficiency and current density of VRBs. Since its first presence, the energy efficiency of a VRB cell has improved from 75% [15] to more than 90%, and the current density has improved from 40 mA/cm² [15] to 400 mA/cm² [16]. This improved performance is achieved through recent advances in the electrode and membrane, such as thermal [17] or chemical treatments for the electrode to enhance its catalytic activity [18], and carbon materials coated onto the surface of the electrode [19,20] to increase electrode's surface area. Optimizations of the flow field within the electrode have also been studied [21] to enhance the mass transfer in the porous electrode and minimize cross-over of the electrolytes through the ion-selective membrane [22]. Although the performance of lab-scale VRBs has drastically improved over the past few decades, VRBs are not yet widely used in the current energy systems, primarily due to a lack of practical VRB dispatch strategies, especially electrolyte flow rate control strategies, and a deep understanding of the cost-effectiveness of VRBs in a variety of applications [23].

Previous studies have investigated the effects of the electrolyte flow rate on the performance of VRBs. Generally, the electrolyte flow rate can influence the mass transfer of active species, the

temperature rise of electrolytes, and the pump power consumption. First, since convection is the leading mechanism for the mass transfer of the active species through the porous electrode [16], the electrolyte flow rate plays a critical role in determining the change in the concentration of the vanadium ions, and thus the concentration overpotential. Li and Hikihara argued that the concentration variation of the vanadium ions should be synchronously determined by the chemical reactions and the electrolyte flow rate [24]; the authors proposed a transient model for describing the dynamic concentration change of the vanadium ions in the tanks and cells under constant flow rates [24]. Second, the electrolyte flow rate of VRBs can also significantly influence the temperature distribution and temperature rise of a VRB cell. Al-Fetlawi et al. found that a large electrolyte flow rate was demanded to render a uniform temperature distribution within a cell, a higher coulombic efficiency, and less hydrogen evolution [25]. Their conclusions were drawn from a two-dimensional, numerical study based on a series of fundamental models that described the mass transfer, electrochemical kinetics, and heat generation resulting from activation loss, electrochemical reactions, and ohmic resistances [25]. Shah et al. advanced this study and developed a dynamic unit cell model for VRBs, which was able to accurately and rapidly predict the performance of a VRB cell (such as the state of charge and open-circuit cell voltage) with given operating conditions [26]. Tang et al. further added the effects of the self-discharge reaction [27], shunt loss [28], and the heat dissipation of the stacks, pipes, and tanks [29] to the VRB thermal model. In addition, threedimensional models were also developed for investigating the effects of the electrolyte flow rate on the temperature distribution

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