



Dynamic thermal-hydraulic modeling and stack flow pattern analysis for all-vanadium redox flow battery



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HIGHLIGHTS

- A dynamic thermal-hydraulic model is developed for different stack flow patterns.
- The flow rate inhomogeneity and reversible entropic heat are included in the model.
- The model is benchmarked by experiments with mean relative error of 5.85%.
- The battery performance is significantly influenced by the stack flow patterns.
- The serpentine–parallel pattern is optimal to enhance the battery performance.

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ABSTRACT

The present study focuses on dynamic thermal-hydraulic modeling for the all-vanadium flow battery and investigations on the impact of stack flow patterns on battery performance. The inhomogeneity of flow rate distribution and reversible entropic heat are included in the thermal-hydraulic model. The electrolyte temperature in tanks is modeled with the finite element modeling (FEM) technique considering the possible non-uniform distribution of electrolyte temperature. Results show that the established model predicts electrolyte temperature accurately under various ambient temperatures and current densities. Significant temperature gradients exist in the battery system at extremely low flow rates, while the electrolyte temperature tends to be the same in different components under relatively high flow rates. Three stack flow patterns including flow without distribution channels and two cases of flow with distribution channels are compared to investigate their effects on battery performance. It is found that the flow rates are not uniformly distributed in cells especially when the stack is not well designed, while adding distribution channels alleviates the inhomogeneous phenomenon. By comparing the three flow patterns, it is found that the serpentine–parallel pattern is preferable and effectively controls the uniformity of flow rates, pressure drop and electrolyte temperature all at expected levels.

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1. Introduction

Although fossil fuels are not a clean energy resource because of the serious pollutant emission, coal-fired energy has played a dominant role in the electrical power generation industry for a long time [1,2]. Renewable energy has been viewed as the promising substitute for coal-fired energy during the past years because it can save the limited fossil fuels while reducing pollution and greenhouse gas emissions. The intermittent nature of renewable energy, however, has posed a rigorous challenge for widespread application. Recent advances and developments in large-capacity batteries

have made it possible for renewable energy to be used in a continuous and steady way [3,4]. Among the multitude of large-capacity batteries, the all-vanadium redox flow battery (VRB) proposed by Skyllas-Kazacos and co-workers [5,6] in the University of New South Wales has been viewed as the most promising. VRBs have also been successfully commercialized in many countries for the unique advantages of elimination of cross contamination, independent capacity and output power design, tolerance to deep discharge, high energy efficiency and long life cycle [6–9].

Thermal modeling is a valuable tool that should be considered for VRB design and operation. For one reason, the electrolytes should be strictly controlled within a specific temperature range for the battery to work efficiently [10]. For instance, for typical electrolytes with 1.8–2 M vanadium sulfate in 2.5–3 M sulfuric acid,

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Nomenclature		ΔS_r^\ominus	standard molar reaction entropy ($\text{J K}^{-1} \text{mol}^{-1}$)
A	surface or cross-section area (m^2)	T	temperature (K)
a	sign factor	t	time (h)
c_p	specific heat of electrolyte ($\text{J kg}^{-1} \text{K}^{-1}$)	V	volume (L)
c	concentration of species (mol L^{-1})	w	width (m)
d	diameter (m)	x	characteristic length (m)
D_h	hydraulic diameter (m)	z	number of moles of electrons exchanged in a reaction
d_f	mean fiber diameter of electrode (m)	<i>Greek symbol</i>	
E^\ominus	standard electrode potential (V)	μ	dynamic viscosity (Pa s)
F	Faraday's constant (C mol^{-1})	ϵ	porosity of graphite felt electrode
f	friction resistance coefficient	θ	thickness (m)
g	acceleration due to gravity (m s^{-2})	ρ	density (kg m^{-3})
Gr	Grashof number	β	volumetric thermal expansion coefficient
ΔG_r^\ominus	standard molar Gibbs free reaction enthalpy (J mol^{-1})	γ	activity coefficient
ΔH_r^\ominus	standard molar reaction enthalpy (J mol^{-1})	<i>Subscript</i>	
h	overall heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)	c	distribution channels
L	length (m)	com	flow combination
I	current (A)	e	electrode
K_p	permeability coefficient	ec	electrode with channels on surface
K_{ck}	Carman–Kozeny constant	f	fluid
K	resistance coefficient	i	inner surface
k	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	in	inlet
N	number of cells	m	manifold channel
Nu	Nusselt number	mi	input manifold channel
P	power (W)	mo	output manifold channel
p	pressure (Pa)	o	outer surface
Δp	pressure drop (Pa)	p	pipe
Pr	Prandtl number	pi	pipe connecting the inlet of stack and outlet of tank
Q	operating flow rate ($\text{cm}^3 \text{s}^{-1}$)	po	pipe connecting the outlet of stack and inlet of tank
q	flow rate in cells ($\text{cm}^3 \text{s}^{-1}$)	r	rib
R	gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)	sep	flow separation
r	radius (m)	s	stack
Ra	Rayleigh number	t	tank
Re	Reynolds number	w	wall
R_c	stack resistance during charge (Ω)	+	positive side
R_d	stack resistance during discharge (Ω)	–	negative side
SOC	state of charge (%)		

thermal precipitation of V^{5+} happens when the temperature is higher than 40°C over extended periods, while precipitation of V^{2+}/V^{3+} occurs when the electrolyte temperature drops below 5°C [11]. Battery efficiency cannot be confirmed and the precipitation can even block the electrolyte channels if the temperature is left uncontrolled. Although precipitation can be minimized by lowering the vanadium ion concentration below 1.8 M, this leads to a reduced energy density that is often undesirable. For this purpose, a temperature control system is highly desirable for the high-efficiency operation of the VRB, although such a battery control system can only be established based on the accurate on-line prediction of electrolyte temperature. Furthermore, accurate temperature prediction serves as the requisite for modeling the electrical behavior of the VRB, which is vital for interfacing the battery with other power electronic devices [12]. This is because of many crucial parameters in electrical models, for example electrode potential, cell resistance and SOC determination are all related to the electrolyte temperature [13].

Though of great importance, studies on thermal modeling of VRB have been considerably limited. A two-dimensional numerical model was established by Al-Fetlawi et al. [14]. Such a numerical model was able to acquire detailed temperature distribution information in the battery and is helpful for the battery design. The

high calculation complexity and long simulating times, however, was not suitable for the dynamic control of electrolyte temperature. Tang et al. [15] first proposed a dynamic thermal model considering the energy and mass conservation. The electrolyte temperatures under both constant and varying surrounding temperature were studied. Further, the effect of self-discharge reactions was added to the model to acquire a more reasonable solution of temperature [16]. One limitation was that the reversible entropic heat [20] was simplified and incorporated into a cell resistance term. In more recent papers, Tang et al. [17,18] modeled the effect of shunt current and flow rate on battery efficiency, stack temperature, pressure losses, etc. In the earlier work, a dynamic model was built by considering the impacts of pump energy losses on the electrolyte temperature [19] but several issues were still expected to be improved. The entropic heat from chemical reaction was considered, but this heat source was simplified as enthalpy change of the electrode reaction, which reduced the accuracy of the simulations. Another essential limitation of the earlier dynamic models was that the effect of stack flow patterns was not considered and flow rate was assumed to be uniformly distributed in each cell, which actually deviated from the practical situation. Therefore, the earlier dynamic models are not adequate to be used in the practical stack design because significant non-uniform distribution of flow rates

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