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Numerical investigations of flow field designs for vanadium redox flow batteries

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HIGHLIGHTS

- The performance of VRFBs with different flow fields is numerically simulated.
- A power-based efficiency is defined and calculated for different flow fields.
- An optimal flow rate exists for each type of flow field.
- The serpentine flow field appears to be more suitable for VRFBs.

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ABSTRACT

As a key component of flow batteries, the flow field is to distribute electrolytes and to apply/collect electric current to/from cells. The critical issue of the flow field design is how to minimize the mass transport polarization at a minimum pressure drop. In this work a three-dimensional numerical model is proposed and applied to the study of flow field designs for a vanadium redox flow battery (VRFB). The performance of three VRFBs with no flow field and with serpentine and parallel flow fields is numerically tested. Results show that when a flow field is included a reduction in overpotentials depends not only on whether a flow field can ensure a more even distribution of electrolytes over the electrode surface, but also on whether the flow field can facilitate the transport of electrolytes from the flow field towards the membrane, improving the distribution uniformity in the through-plane direction. It is also shown that the pumping power varies with the selection of flow fields at a given flow rate. To assess the suitability of flow fields, a power-based efficiency, which takes account of both the cell performance and pumping power, is defined and calculated for different flow fields at different electrolyte flow rates. Results indicate that there is an optimal flow rate for each type of flow field at which the maximum efficiency can be achieved. As the cell with the serpentine flow field at the optimal flow rate shows the highest energy-based efficiency and round-trip efficiency (RTE), this type of flow field appears to be more suitable for VRFBs than the parallel flow field does.

1. Introduction

Renewable energies like solar and wind are among a few of the central topics of our time. However, the random and intermittent nature of renewable energy affects the final quality of power output. Energy storage is the key technology to solve this problem [1]. Among various existing energy-storage techniques, the all-vanadium redox flow battery (VRFB) offers the promise for large scale energy storage due to its unique features: tolerance to deep discharge without any risk of damage, long cycle life, active thermal management and independence of energy and power ratings [2–6].

Although progress has been made over the past decades, significant technical challenges, including slow electrochemical kinetics in the positive electrode, low solubility of active species in electrolytes and ions crossover through the polymer membrane, are the barriers that prevent VRFBs from widespread commercialization. To address these issues, previous efforts include decorating electrodes with metal or inorganic elements [7–9] or find alternative electrode materials [10–12], adding additives to electrolyte to improve its solubility [13–15], as well as modifying existing membranes and searching for alternatives [16–20], have been widely reported. The design of flow field of VRFBs is also closely related to the above mentioned technical issues. However, the studies on the flow field design for VRFBs remain limited.

The flow field serves four functions [21–24]: to distribute electrolytes on the electrode surface, to apply/collect electric current

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Nomenclature

A_V	specific surface area of the porous electrode ($m^2\ m^{-3}$)
c	concentration ($mol\ m^{-3}$)
D	diffusivity ($m^2\ s^{-1}$)
d_f	mean fibre diameter (m)
E_1	negative open circuit potential (V)
E_2	positive open circuit potential (V)
E_{cell}	cell voltage (V)
E^0	equilibrium potential (V)
F	Faraday constant ($C\ mol^{-1}$)
I	current density ($A\ m^{-2}$)
$\vec{i}_m$	current density in the solid matrix ($A\ m^{-2}$)
$\vec{i}_s$	current density in the electrolyte solution ($A\ m^{-2}$)
j_1	negative electrode current density ($A\ m^{-3}$)
j_2	positive electrode current density ($A\ m^{-3}$)
K	permeability of porous material (m^2)
K_{CK}	Carman–Kozeny constant
k_1	standard reaction rate constant for negative reaction ($m\ s^{-1}$)
k_2	standard reaction rate constants for positive reaction ($m\ s^{-1}$)
k_m	local mass transfer coefficient ($m\ s^{-1}$)
l_{mem}	membrane thickness (m)
$\vec{N}$	molar flux ($mol\ m^{-2}\ s^{-1}$)
$\vec{n}$	unit normal vector at a domain boundary
P	power (W)
p	pressure (Pa)
Q	volumetric flow rate ($ml\ s^{-1}$)
R	gas constant, 8.314 ($J\ mol^{-1}\ K^{-1}$)
$\dot{R}$	source term in species conservation equation ($mol\ m^{-3}\ s^{-1}$)
R_{cell}	cell resistance ($\Omega\ m^2$)
S	surface area of the electrode
T	temperature (K)
U	uniformity factor
W	work (J)
$\vec{u}$	superficial velocity ($m\ s^{-1}$)
x	coordinate (m)
y	coordinate (m)
z	valence of ion

Greek

α_+	anodic transfer coefficients
α_-	cathodic transfer coefficients
ε	porosity of porous electrode
ψ	efficiency
η	over-potential (V)
μ	ionic mobility ($m^2\ V^{-1}\ s^{-1}$)
ν	kinematic viscosity ($m^2\ s^{-1}$)
ρ	density ($kg\ m^{-3}$)
σ_m	conductivity of the solid matrix ($S\ m^{-1}$)
σ_{mem}	conductivity of polymer electrolyte membrane ($S\ m^{-1}$)
ϕ_m	potential in the solid matrix (V)
ϕ_{mem}	potential in the membrane (V)
ϕ_s	potential in the electrolyte solution (V)

Superscripts

0	initial value
e	ending value
eff	effective value
s	value at the pore surface of porous electrode

Subscripts

1	negative electrode
2	positive electrode
char	charge
disch	discharge
H^+	proton
H_2O	water
in	inlet
m	solid matrix
mem	membrane
out	outlet
s	solution
HSO_4^-	bisulfate ion
V(II)	V^{2+} ion
V(III)	V^{3+} ion
V(IV)	VO^{2+} ion
V(V)	VO_2^+ ion

to/from the cells, to provide a structural support for the electrode material and to facilitate heat management. Among these functions, the requirements for the latter three are relatively readily met. However, to design a flow field that meets the requirement for the first function is much more challenging. To make a VRFB efficient, it is essential to minimize the mass transfer polarization over the entire electrode. To this end, a uniform distribution of electrolytes on the electrode surface is required. However, the uniformity of electrolytes on the electrode surface is usually achieved at the cost of high flow rates, requiring a higher pumping power, which will reduce the overall efficiency of flow batteries. Hence, the key issue associated with the flow field design is how to minimize the mass transport polarization at a minimum pressure drop through the flow field.

A few experimental investigations into flow fields of VRFBs have been reported [25–27]. Zhu et al. [25] investigated the effects of two different flow fields, one with a flow-pass pattern while the other with a flow-through pattern, on the performance of a VRFB. The experimental results suggested that the flow-through pattern tended to increase the electrode effective active area and to enhance the uniformity of liquid electrolyte, resulting in an improvement in the energy efficiency by up to 5%. Recently, Zawodzinski et al. [26–28] introduced a so-called zero-gap cell architecture with a serpentine flow field, enabling the peak power density to be 767 mW cm^{-2}, which is significantly higher than the conventional cell configuration; the enhancement of the cell performance was attributed to the enhanced mass transport and reduced internal resistance.

Numerical modeling and simulation can provide insight to the flow field design. To the best of our knowledge, no numerical investigations into the effect of flow fields on the performance of VRFBs have been reported. In this work, a three-dimensional model based on computational fluid dynamics and electrochemical reactions is developed. With this model, the effects of flow field design (flow-through with no flow field, with serpentine and parallel flow fields, as shown in Fig. 1) on the distributions of ion concentrations, local overpotential and local current density at various flow rates, as well as on the system efficiency are investigated and the flow field design that is more suitable for VRFBs is identified.

2. Mathematical model

Consider a typical single VRFB consisting of a Nafion membrane, two graphite electrodes separated by the membrane and two