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Effect of flow-field structure on discharging and charging behavior of hydrogen/bromine redox flow batteries

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ABSTRACT

Designing and optimizing the flow-field structure for the liquid phase Br_2/HBr electrolyte solution of H_2/Br_2 redox flow batteries (RFBs) is important for improving cell performance. In this study, two electrolyte flow modes, i.e. the flow-by and flow-through modes, are simulated by using a three-dimensional H_2/Br_2 RFB model. The model is first applied to real-scale H_2/Br_2 cell geometries and then validated against the experimental polarization curves acquired using the two different flow modes. The model predictions compare well with the experimental data and further highlight the advantages of using the flow-through mode relative to the flow-by mode. Detailed multi-dimensional contours of the electrolyte flow velocity and key species distributions reveal that more uniform diffusion and stronger convective transport are achieved by using the flow-through mode, which alleviates the ohmic loss associated with charge transport in the Br_2 electrode.

1. Introduction

With the growing importance of grid-scale energy storage, the hydrogen/bromine redox flow battery (RFB) has received much attention due to its superior regenerative behavior and lower electrolyte cost. Recently, a high power density of 1.4 W cm^{-2} and slow degradation of the RFB performance over 10,000 h were reported for 10–25 cm^2 lab-scale cells [1–5]. Although bromine (Br_2) is highly corrosive to most materials, several candidate materials compatible with Br_2 solutions have been identified and employed for H_2/Br_2 cell and system construction. A brief review of Br_2 resistant materials was provided by Cho et al. [6]. Safety is another concern due to the toxicity of Br_2 (including inhalation and skin contact concerns), and thus additional safety measures must be considered including double tank construction, neutralization compounds, appropriate protective wear during servicing, and active monitoring. However, Br_2 has been used and deployed in these systems as well as Zn-Br; thus while additional safety measures are required, it is a solvable issue.

As shown in Fig. 1, in the hydrogen/bromine RFB system, gaseous hydrogen and an aqueous solution of Br_2 and hydrobromide (HBr) are fed into the negative and positive electrodes, respectively. These two electrodes are separated by a thin proton exchange membrane (PEM) such as DuPont's Nafion®. During H_2/Br_2 RFB operations, the cell performance is mainly limited by the positive electrode wherein electrochemical and transport processes of aqueous Br_2/HBr solution are far more sluggish than those of gaseous hydrogen in the negative electrode. Besides the activation and concentration overpotential in the positive electrode, the ohmic loss due to ion transport through the membrane can be a significant contributor to the overall voltage drop, if a high degree of membrane dehydration occurs. A level of membrane dehydration is closely related to the crossover fluxes of water and bromine species, i.e. altered between charge and discharge as well as by the magnitude of state-of-charge (SOC).

Several design issues related to sealing and manifolding may arise, particularly when the cell is scaled up to larger sizes and stacks for grid-level energy storage. Flow-field design and optimization become more critical in facilitating the distribution of reactants and removing products in large-scale cells. Xu et al. [7] numerically compared three different flow field designs for a 100 cm^2 vanadium RFB. In general, using serpentine flow field

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Nomenclature

A	cross-sectional area, m^2
a	specific surface area, m^{-1}
bFFP	bromine flow field plate
bPM	bromine porous media
C	molar concentration, $mol\,m^{-3}$
C_{KC}	Kozeny-Carman constant
D	diffusion coefficient, $m^2\,s^{-1}$
d_f	fiber diameter, m
E_0	thermodynamic equilibrium potential, V
F	Faraday's constant, 96485 $C\,mol^{-1}$
hCL	hydrogen catalyst layer
hFFP	hydrogen flow field plate
hPM	hydrogen porous media
i	current density, $A\,m^{-2}$
j	transfer current density, $A\,m^{-3}$
K	permeability, m^2
M	molecular weight, $kg\,mol^{-1}$
$\vec{N}$	species flux, $mol\,m^{-3}\,s^{-1}$
n_d	electro-osmotic drag coefficient
P	pressure, Pa
Q	volumetric flow rate, $m^3\,s^{-1}$
R	universal gas constant, 8.314 $J\,mol^{-1}\,K^{-1}$
r_{PM}	pore radius in porous media, m
S	source/sink term
T	temperature, K
u	velocity, $m\,s^{-1}$
V_{cell}	cell voltage, V, or velocity, $m\,s^{-1}$
vf_i	volume fraction of species i
z	valence

Greek symbols

α	transfer coefficient
ε	porosity
η	overpotential, V
κ	proton conductivity, $S\,m^{-1}$
μ	viscosity, $kg{\cdot}m^{-1}\,s^{-1}$
ρ	density, $kg{\cdot}m^{-3}$
σ	electronic conductivity, $S\,m^{-1}$
τ	viscous shear stress, $N\,m^{-2}$ or tortuosity
ϕ	potential, V

Subscript

0	equilibrium or initial value
a	anodic reaction value
b	bromine electrode side
c	cathodic reaction value
e	electrolyte
eq	equilibrium state
FFP	flow field plate
h	H_2 electrode side
$\underline{i}$	species i
in	inlet
mem	membrane
s	solid (electronic)
u	momentum

Superscript

*	remain
$bulk$	bulk value
eff	effective
g	gas state
s	surface value
$xover$	crossover

requires a higher pumping power but helps to enhance the uniformity of liquid electrolyte flow and consequently reduce overpotential in both negative and positive electrodes. As the electrolyte rate increases, however, the higher power-based efficiency was achieved with the porous electrode without flow field (namely flow-through mode), which implies that the flow-through cell configuration may be well suited for high power H_2/Br_2 RFB that requires high electrolyte flow rate.

Cho et al. [8] evaluated two different flow-field configurations (flow-by and flow-through modes) for supply of aqueous Br_2/HBr to cells with an active area of 10 cm^2. In the flow-by mode, the aqueous Br_2/HBr mixture is first fed into the flow channels and then diffuses toward the reaction site in the porous electrode, whereas the Br_2/HBr electrolyte directly penetrates through the porous electrode in the flow-through mode. Roughly, 23% improvement in the maximum power density was reported by using the flow-through mode instead of the flow-by mode. The enhanced performance achieved with the former was attributed to the stronger convective electrolyte flow in the Br_2 electrode driven by the flow-through mode, leading to enhanced removal of the discharge product (HBr) from the cell, thereby minimizing membrane dehydration and proton resistance. Those results clearly illustrated the substantial impact of the flow-field design on the performance of H_2/Br_2 RFBs.

To scale up the lab-scale cell (a few cm^2) to a practical large-scale cell for grid-level energy storage applications (from several hundreds to thousands of cm^2), three-dimensional (3-D) modeling and real-scale simulations are required to fully elucidate the complex electrochemical and transport phenomena occurring in the real-scale cells. This understanding is key to successful design and operation of H_2/Br_2 RFB systems. In this study, a 3-D, transient H_2/Br_2 RFB model developed in a previous study [9] is applied to a real-scale cell with an active area of 10 cm^2. In order to reduce the computational turnaround time involved in a large numerical mesh with millions of grid points, the 3-D H_2/Br_2 RFB code is parallelized for parallel computing. Emphasis is placed on exploring the effects of the electrolyte flow mode in the Br_2 electrode (i.e. flow-by vs. flow-through mode) on the multi-dimensional reactant and product distributions, and the resultant voltage loss and cell performance. Such an elaborate simulation tool for the prediction of electrochemical performance and transport phenomena is highly desirable in the design and engineering of large-scale H_2/Br_2 RFBs.

2. Numerical model

2.1. Model assumptions

The 3-D H_2/Br_2 RFB model developed previously [9,10] accounts for the redox reactions of H_2 and Br_2/HBr solutions and the resulting species transport inside the cell. The assumptions made in the model are as follows:

1) Gaseous or aqueous flow is incompressible and laminar because of the low flow velocity.
2) The porous electrodes are characterized by effective porosity and permeability.
3) The cell is assumed to be isothermal during charge and discharge.
4) The gas mixtures obey the idea gas law due to low pressure.
5) The gravitational effect is neglected.
6) The dilute solution theory is employed to describe species transport.
7) The thickness of membrane is assumed to be constant, neglecting the effect of membrane swelling/shrinking due to its hydration/dehydration during cell operations.