Journal of Power Sources 384 (2018) 295–302

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Redox flow batteries with serpentine flow fields: Distributions of electrolyte flow reactant penetration into the porous carbon electrodes and effects on performance

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HIGHLIGHTS

- A three-dimensional model of serpentine flow fields in a flow battery.
- Flow distributions at the flow field-porous carbon electrode interface.
- Quantified electrolyte penetration into the porous carbon electrode.
- Maximum current density estimate based on reactant availability.
- Effects of electrode thickness and porosity on maximum current density.

ARTICLE INFO

Keywords:
Flow field design
Electrolyte streamlines
Limiting current density
Maximum current density
Electrode performance

ABSTRACT

Redox flow batteries with flow field designs have been demonstrated to boost their capacities to deliver high current density and power density in medium and large-scale energy storage applications. Nevertheless, the fundamental mechanisms involved with improved current density in flow batteries with serpentine flow field designs have been not fully understood. Here we report a three-dimensional model of a serpentine flow field over a porous carbon electrode to examine the distributions of pressure driven electrolyte flow penetrations into the porous carbon electrodes. We also estimate the maximum current densities associated with stoichiometric availability of electrolyte reactant flow penetrations through the porous carbon electrodes. The results predict reasonably well observed experimental data without using any adjustable parameters. This fundamental work on electrolyte flow distributions of limiting reactant availability will contribute to a better understanding of limits on electrochemical performance in flow batteries with serpentine flow field designs and should be helpful to optimizing flow batteries.

1. Introduction

Rechargeable redox flow batteries are considered as promising candidates for medium and large-scale stationary energy storage applications [1,2]. The electric energy stored by flow battery systems can be used to firm up intermittent renewable energy resources, and it can help to deliver consistent electricity to improve the stability of the electric grid [3–6]. During recent decades, several types of flow batteries have emerged: all-vanadium [7,8], all-iron [9–11], zinc-poly-iodide [12], semi-solid lithium ion [13,14], hydrogen-bromine [15,16], organic [17,18], and others. The merits of lower capital costs, eco-friendly, long-term life and higher electrochemical performance of flow batteries are desired [1–6]. Fundamental studies on electrodes [19], electrolytes [20], membrane [21,22] and cell design [4] have been reported. Zawodzinski et al. [23,24] first reported a vanadium flow battery with a “zero-gap” serpentine flow field architecture. Higher current density and power density were observed in their cell with this flow field design, which can drive down capital costs of the energy storage system. Since then, other work on flow batteries with flow field-electrode designs have appeared in the literature [25–34]. Various

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https://doi.org/10.1016/j.jpowsour.2018.03.001
Received 8 January 2018; Received in revised form 24 February 2018; Accepted 1 March 2018
0378-7753/

Nomenclature

A	area of ion selective membrane (cm^2)
BC	boundary condition
c	concentration (mol cm^{-3})
cr	compression ratio
C	constant
E	voltage (V)
ΔE	voltage drop (V)
F	Faraday constant (96,485 C $equiv^{-1}$)
i	current density (A cm^{-2})
k	permeability of the porous electrode (m^2)
L	length (cm)
n	number of electrons transferred in reactions (equiv mol^{-1})
P	pressure (Pa)
Q	volumetric flow rate (cm^3 min^{-1} or cm^3 s^{-1})
t	thickness (cm)
T	working temperature (K)
U	X-direction velocity (cm s^{-1})
V	Y-direction velocity (cm s^{-1})
W	Z-direction velocity (cm s^{-1})
W	width (cm)
X	X-direction (cm)
Y	Y-direction (cm)
Z	Z-direction (cm)

Greek symbols

ε	porosity
μ	dynamic viscosity (Pa s)
ρ	density of electrolyte flow (kg cm^{-3})
Ω	interface
σ	conductivity (mS cm^{-1})
η	round-trip efficiency

Subscripts

avg	average value
cc	corner channel
e	electrolyte phase
f	flow channel domain
fp	flow passage
in	inlet
lim	limiting
max	maximum
o	original
ocv	open circuit voltage
ohm	ohmic loss
p	porous electrode domain
s	solid phase
tot	total
-z	component in the –Z direction

effects on cell performance were studied: electrode structures [27], flow field architectures [28], flow distributions and pressure drops [29], mass transfer limits [30], etc. An explanation of the improved electrochemical performance in flow batteries with serpentine flow field designs was reported in our previous work [31–34]. A two-dimensional numerical model [32] was presented along a single flow channel of the serpentine flow field. The pressure difference between the single flow channel and porous domain created a driving force for electrolyte flow to penetrate into the porous carbon electrode. Also, a simplified analytical model [33] was reported to estimate the volumetric flow penetration into the porous carbon electrode as fully developed flow was approached. A maximum current density was estimated which corresponds with 100% utilization of reactant flow penetration into the porous carbon electrode. However, an "adjusted" high permeability of porous carbon electrode was required to predict experimentally observed limiting current densities.

In this report, we present several further important aspects beyond our previous work [31–34]: (1) extend a two-dimensional model to a three-dimensional model of an actual serpentine flow field over porous carbon electrode; (2) account for forced convective flow penetration into the porous carbon electrode beneath the landings/ribs enhanced by pressure difference between the adjacent flow channels; (3) assess several models to correlate porosity and permeability of the porous electrode; (4) demonstrate reasonable agreement between this model and experimental data using a more realistic permeability of the porous carbon electrode instead of an "adjusted" one, and (5) discuss the effects of electrode thickness, entrance volumetric flow rate and porosity of porous carbon electrode on maximum current density. Lastly, the maximum current density estimated by this three-dimensional model was compared to the experimental data reported in vanadium flow batteries with serpentine flow fields. This work contributes to the fundamental understanding of serpentine flow field designs on electrochemical performance and should be helpful to optimizing flow battery designs near the future.

2. Flow cell with a serpentine flow structure

The half-cell components of a flow battery with a serpentine flow channel over carbon paper electrode architecture are described in Fig. 1 (a) and (b). This half-cell structure was used as an example to model the observed limiting current density by estimating the amount of electrolyte flow reactant penetrating into the porous electrode from the serpentine flow channel. The half-cell structure consists of a current collector (2), a graphite plate engraved with a serpentine flow field (3), a gasket (4), a porous carbon electrode (5), and an ion selective membrane (6). The electrolyte in the tank reservoir is circulated by a pump through the serpentine flow field and over the porous electrode. The cross-section views of the serpentine flow channel over the porous carbon electrode are shown in Fig. 1 (b): single flow passage and porous electrode (see view 1) and adjoin flow passages with landings/ribs over porous the electrode (see view 2). The three-dimensional geometry of the serpentine flow field with landings/ribs over the porous electrode used in this mathematical model is described in Fig. 1 (c) (three-dimensional *XYZ* view). A serpentine flow field over the porous carbon electrode is simulated as shown in Fig. 1 (d) (two-dimensional *XY* view). The serpentine flow field consists of eleven flow passages (*fp*) and ten corner channels (*cc*), see Fig. 1(d). This geometry (and dimensions) represents a typical cell architecture reported in the literature [24]. The flow passages are designated as *fp*#1 through *fp*#11 and corner channels are designated as *cc*#1 through *cc*#10.

3. Modeling approach

The flow field considered in this work is composed of a serpentine flow channel with eleven flow passages (*fp*) and ten corner channels (*cc*) over a porous carbon electrode in a vanadium flow battery with a "zero-gap" serpentine flow structure. The electrolyte flow dynamics in the flow field are governed by the Navier-Stokes equations (see details in supplementary materials). A macroscopic model known as "Brinkman-Darcy" (see details in supplementary materials), which incorporates a flow "permeability" is used to capture flow physics in the porous carbon electrode. The corresponding component of the flow