Electrochimica Acta 223 (2017) 124–134

Contents lists available at ScienceDirect

Electrochimica Acta

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

# Mathematical Modeling of Electrolyte Flow in a Segment of Flow Channel over Porous Electrode Layered System in Vanadium Flow Battery with Flow Field Design

Xinyou Ke[a,b,e,*], Joseph M. Prahl[a], J. Iwan D. Alexander[a,c], Robert F. Savinell[d,e]

[a] Department of Mechanical and Aerospace Engineering, Case Western Reserve University, Cleveland, OH 44106, United States
[b] John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02318, United States
[c] School of Engineering, University of Alabama at Birmingham, Birmingham, AL 35294, United States
[d] Department of Chemical and Biomolecular Engineering, Case Western Reserve University, Cleveland, OH 44106, United States
[e] Electrochemical Engineering and Energy Laboratory, Case Western Reserve University, Cleveland, OH 44106, United States

ARTICLE INFO

*Article history:*
Received 5 July 2016
Received in revised form 27 November 2016
Accepted 3 December 2016
Available online 6 December 2016

*Keywords:*
flow battery with flow field model
interface flow distributions
pressure distributions
volumetric flow penetrations
ideal parabolic and plug flow inlet boundary conditions

ABSTRACT

In this work, a two-dimensional mathematical model is developed to study the flow patterns and volumetric flow penetrations in a segment of flow channel over porous electrode layered system in vanadium flow battery with flow field design. The flow distributions at the interface between the flow channel and porous electrode are examined. It is found that the non-linear pressure distributions can distinguish the interface flow distributions under the ideal plug flow and ideal parabolic flow inlet boundary conditions. Nevertheless, the volumetric flow penetration within the porous electrode beneath the flow channel through the integration of interface flow velocity reveals that this value is identical under both ideal plug flow and ideal parabolic flow inlet boundary conditions. The volumetric flow penetrations under the advection effects by both flow channel and landing/rib are estimated. The maximum current density achieved in a flow battery with a flow field architecture can be predicted based on the 100% amount of electrolyte flow reactant consumption through the porous electrode beneath flow channel and landing/rib. The corresponding theoretical maximum current densities achieved in vanadium flow battery with one and three layers of SGL 10AA carbon paper electrode have reasonable agreement with experimental results under a proper permeability.



## 1. Introduction

Redox flow batteries (RFBs) technologies have been gained unprecedented attention for medium and large-scale energy storage applications [1–3]. In conjunction with electric generation from intermittent renewable energy sources (e.g. wind, tide and solar energy), RFBs are demonstrated to be alternative tools within enabling to improve stability of national grid [4]. Until now, several types of RFBs have been developed, typically such as all-vanadium [5,6], iron-chromium [7,8], all-iron aqueous/all-iron slurry [9], semi-solid lithium [10], etc. Designs of new electrolytes and flow cell architectures attract researchers in the field of flow batteries. The studies on working mechanism of flow batteries are still going on. In this effort, we study the transport mechanism in a typical all-vanadium redox flow battery (all-VRFB) [4,11–13] and one advantage for the VRFB is that species are reversibly consumed in the electrolyte reservoir [5]. Experiments and mathematical modeling are two approaches to study the fundamental insights. Compared with experimental studies, the capital costs and labor effort are reduced at some degree while crucial understanding of transport phenomena still can be achieved through the computational modeling [14,15]. Earlier work on mathematical modeling of redox flow batteries was reported by Newman et al. [16,17] and they proposed a one-dimensional theoretical model to study current distributions and non-uniform kinetic reactions though the porous electrode. Shah et al. [18] developed a two-dimensional vanadium flow battery without flow channel model to study the transport physics including convection, diffusion and migration in the electrode. Subsequently, You et al. [19] studied the parameter effects on the distributions of local reactant concentration, over-potential and current density based on the previous reported two-dimensional flow battery without flow field model [18]. A two-dimensional transient vanadium flow battery without flow field

* Corresponding author.
*E-mail addresses:* xinyouke@gmail.com, xxk4@case.edu (X. Ke).

http://dx.doi.org/10.1016/j.electacta.2016.12.017
0013-4686/

**Nomenclature**

| | |
|---|---|
| $A$ | area integration |
| $BC$ | boundary condition |
| $c$ | concentration (mol cm$^{-3}$) |
| $k$ | permeability of the porous electrode (cm$^2$) |
| $L$ | length (cm) |
| $P$ | pressure (Pa) |
| $<P>$ | average pressure (Pa) |
| $Q$ | volumetric flow rate (ml min$^{-1}$ or cm$^3$ s$^{-1}$) |
| $r$ | distance between adjacent flow channels (cm) |
| $t$ | thickness (cm) |
| $u$ | velocity along the $X$-direction (cm s$^{-1}$) |
| $<u>$ | velocity along the average $X$-direction (cm s$^{-1}$) |
| $v$ | velocity along the $Y$-direction (cm s$^{-1}$) |
| $<v>$ | average velocity along the $Y$-direction (cm s$^{-1}$) |
| $w$ | width (cm) |
| $X$ | $X$-direction |
| $Y$ | $Y$-direction |

Greek symbols

| | |
|---|---|
| $\varepsilon$ | porosity |
| $\mu$ | dynamic viscosity (Pa•s) |
| $\upsilon$ | kinematic viscosity (cm$^2$ s$^{-1}$) |
| $\rho$ | density of electrolyte fluid (g cm$^{-3}$) |
| $\Sigma$ | interface |

Subscripts

| | |
|---|---|
| $avg$ | average value |
| $cf$ | between current collector and flow channel |
| $e$ | entrance |
| $f$ | flow domain |
| $fc$ | flow channel |
| $fp$ | between flow channel and porous electrode |
| $in$ | inlet |
| $i$ | number (1, 2, 3, 4, 5 and 6) |
| $lc$ | landing/rib-corner channel |
| $p$ | porous domain |
| $pm$ | between porous electrode and ion selective membrane |

Dimensionless number

| | |
|---|---|
| $P_f^*$ | $P_f (\rho u_{in}^2)^{-1}$ |
| $<P_p>^*$ | $<P_p>(\rho u_{in}^2)^{-1}$ |
| $u_f^*$ | $u_f u_{in}^{-1}$ |
| $<u_p>^*$ | $<u_p>u_{in}^{-1}$ |
| $v_f^*$ | $v_f u_{in}^{-1}$ |
| $<v_p>^*$ | $<v_p>u_{in}^{-1}$ |
| $X^*$ | $XL^{-1}$ |
| $Y^*$ | $Y(t_f+t_p)^{-1}$ |
| $Re$ | Reynolds number ($\rho u_{in} t_f \mu^{-1}$) |

model was developed by Knehr et al. [15]. The species' crossovers at the interface boundary between the electrode and membrane were studied. The worked done by Newman et al. [16,17], Shah et al. [18], You et al. [19] and Knehr et al. [15] were on flow batteries without flow fields through the felts (e.g. carbon and graphite felts). However, Aaron et al. [20] first reported a vanadium flow cell stack configuration with serpentine flow field over carbon paper electrode. The electrochemical performance (e.g. limiting current density and peak power density) was greatly improved. The thickness of carbon paper electrode (~0.04 cm) [20] used in vanadium flow battery with flow field is much thinner than the graphite felt or carbon felt (typical ~0.3 cm) [18,19] used in the one without flow field. Here, the flow channels, such as serpentine and interdigitated flow fields were evolved from proton exchange membrane fuel cell (PEMFC) design [20,21]. Up to date, few theoretical studies on details of RFBs with flow fields have been reported. Ke et al. [22] developed a macroscopic model of RFBs with a single passage of the serpentine flow channel. Both numerical and analytical flow distributions in the flow channel and porous electrode were studied [23,24]. The first mathematical model for predicting the maximum current density achieved in the flow battery with flow fields was proposed. This maximum current density model is based on the consumption of total flow ion reactants through the porous electrode in the RFBs with flow field designs. The thinner carbon fiber paper electrodes (typical 10AA SGL and Toray paper) used in the RFBs with flow fields (e.g., serpentine and interdigitated flow channels) can reduce ohmic losses compared with the conventional RFBs without flow fields. The electrochemical performance of flow cell with flow field design can be improved. There are two porous electrode configurations of RFBs: (1) the classic RFBs without flow field [14–19] as shown in Fig. 1 (a), the electrolyte flows through a thick electrode and (2) the RFBs with flow field [20–26] as shown in Fig. 1 (b), the electrolyte flows through the flow channel and by-passes into a thinner electrode. The fundamental studies on the flow details in the flow batteries with flow field designs are quite few. The deep mechanism of electrolyte flow reactant penetration into the porous electrode from the flow channel is not well understood. There are two typical experimental approaches to characterize the electrolyte flow dispersion: visualization [27] and residence time distribution (RTD) [28] techniques. The visualization technique can capture the transport process (e.g. streamline) of electrolyte flow and RTD can calculate the time that particles go through the reactors based on the probability function. Although both visualization and RTD approaches are always prior to multiphysics modeling on characterization of flow dispersion, it seems that they have less capabilities of capturing amount of electrolyte flow penetration through the porous electrode. In this study, the amount of electrolyte flow penetration from the flow channel into the porous electrode is concerned. The flow penetration and possible maximum current density achieved based on 100% utilization of electrolyte through the porous electrode is correlated. Thus, the multiphysics modeling approach is preferred to visualization and RTD techniques in this study on electrolyte flow penetration.

The motivation of this work on vanadium flow battery with flow field design over carbon paper electrodes compared with classic one without flow field design through the carbon felts is based on two possible merits: (1) the forced convection through the flow fields can enhance the mass transport through the electrode layer and (2) thinner carbon paper electrode (hundred microns) has lower ohmic loss in contrast to the thicker carbon or graphite felts (several millimeters). In this article, we study the flow patterns in the flow channel and porous electrode to explain the role of the convection consequently mass transfer in the flow batteries with flow field design as shown in Fig. 1 (b). The flow penetration or volumetric flow rate within the porous electrode is studied under both ideal plug flow inlet and ideal parabolic flow inlet boundary conditions. The maximum current density achieved in the flow cell can be estimated by a function of calculated volumetric flow rate within the porous electrode, number of electron transferred, Faraday's constant, ion concentration and contact area between the flow channel and porous electrode. This mathematical model should contribute a certain guidance on performance optimization of flow batteries with flow field designs.