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On the mass transport in membraneless flow batteries with flow-by configuration

Kleber Marques Lisboa [a,*], Renato Machado Cotta [a,b]

[a] Laboratory of Nano- and Microfluidics and Microsystems, LabMEMS, Mechanical Engineering Dept. and Nanoengineering Dept., POLI & COPPE and Interdisciplinary Nucleus for Social Development – NIDES/CT, Universidade Federal do Rio de Janeiro, Cidade Universitária, Cx. Postal 68503, Rio de Janeiro, RJ CEP 21945-970, Brazil
[b] Mechanical Engineering Dept., University College London, UCL, Roberts Building, Torrington Place, London WC1E 7JE, UK[1]

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ABSTRACT

Progress on the analysis of the mass transport phenomena in a membraneless redox flow battery with porous electrodes in flow-by configuration is here reported. A species transport model for a typical redox reactant interacting with a porous electrode is proposed. A hybrid numerical-analytical solution is obtained through the Generalized Integral Transform Technique (GITT), adopting a single domain formulation that includes both the porous and pure fluid regions. The influence of the Reynolds number and the thickness of the electrode on the parameters of interest is theoretically examined. The importance of considering the simultaneous development of flow and mass transport is analyzed, and the presence of the transversal convective flux of species proves to have a significant role on the generation of current inside the electrode. A scaling of the limiting current density with $\sim Re^{0.41}$ is demonstrated and some physical conclusions are drawn. Guidelines for the prevention of crossover are also offered, with increasing Reynolds number and decreasing relative thickness of the electrode having a positive effect, as far as avoiding the mixed potentials effects is concerned. The physical insights attained through the present analysis should add to the efforts in achieving membraneless redox flow batteries with performances comparable to membrane-based devices of similar size.

1. Introduction

The challenge posed by climate change urged the rapid development of renewable energy sources, such as wind and solar. However, the intermittency associated with these power sources prevent the complete substitution of less environmental-friendly alternatives. In this context, the availability of efficient energy storage technologies is crucial to allow the reduction of emissions of certain pollutants from fossil fuels [1,2]. The redox flow battery (RFB) has been under development over the last three decades as an attractive energy storage option [3–5]. The main advantage of this concept is the decoupling of the energy and power densities, with the former being mainly determined by the size of the storage tanks, and the latter being mostly associated with the size of the battery itself. Moreover, deep charge-discharge cycles are possible without damaging the components, which contrasts with solid-state batteries [6].

Besides the large-scale electrical energy storage, new usages for RFBs could arise from the miniaturization and decentralization of individual cells towards specific needs in different fields. The resulting diversification of applications could help RFBs attain lower costs, increasing the likelihood of its widespread usage [7]. One example where the use of RFBs would be a good fit is in electronics. The idea is to use flow battery technology for power delivery to the different electronic components. In fact, a fusing function of the well-studied heat removal [8,9] and power delivery for data centers has been proposed [10] and demonstrated [11]. The basic concept is the use of the flux of electrolytes for both cooling and as energy source for individual electronic components, reducing the number of power connections and total wiring length. The perspective is the overall improvement of the energy efficiency and making more space available for logical connections in data centers [10].

Two strategies can be employed in the miniaturization of RFBs. The first consists in maintaining the constructive characteristics of large scale RFBs, solely reducing the size of its components, which has been successfully applied before [11,12]. The second one takes advantage of the laminar flow regime in channels with small cross-sections to limit the mixture of electrolytes at the interface

* Corresponding author.
E-mail address: kleberlisboa@poli.ufrj.br (K.M. Lisboa).
[1] Present address.

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Nomenclature

c	concentration
u	longitudinal velocity component
v	transversal velocity component
∇	nabla operator: $\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$
h	half of the channel height
h_p	thickness of the porous layer
L^*	channel length
Re	Reynolds number
Da	Darcy number
Pe	Péclét number
Sc	Schmidt number
u_f	fully developed velocity profile
c_{in}	entry concentration profile
x_o	dimensionless channel length
w_p	relative thickness of the porous electrode
d_f	diameter of the pore or the fiber of the electrode
a	specific area of the electrode
k_m	mass transfer coefficient
M	eigenfunction truncation order
N	concentration truncation order

Greek letters

σ	$= d_f/h$
ε	porosity of the electrode
β, υ	eigenvalues corresponding to eigenfunctions ψ and ξ, respectively
ψ	eigenfunction for the concentration
ξ	auxiliary eigenfunction
δ	Kronecker delta

Subscripts and superscripts

i, j, k	order of eigenquantities for the concentration and velocity vector
m, n	order of auxiliary eigenquantities
$\sim$	normalized eigenfunction
$*$	dimensional quantity
T	transpose
b	bulk quantity

between them, enabling the removal of the membrane in RFBs and fuel cells [13–15]. The so-called membraneless co-laminar flow cells are simpler and cheaper to manufacture in comparison with membrane-based ones with similar size, mainly due to the absence of the costly ion-selective membrane [16]. However, membraneless RFBs suffer from low Reynolds diffusion-limited mass transport, severely limiting the overall performance of these devices. Several strategies have been reported for increasing the mass transport performance of membraneless flow cells, from the use of porous carbon electrodes [15,17–19], to the employment of chaotic mixers [20–22]. Disrupting the diffusion-limited transport has the critical side-effect of doing the same to the interface between the two electrolytes, making crossover and mixed potential phenomena more likely. Addressing the two aforementioned issues together strongly benefits the overall performance of membraneless flow cells, leading to a maximum power density of 0.925 W/cm^2 recently reported in the literature [23]. This power density is on the same order magnitude to the ones attained with membrane-based microfluidic RFBs [11,12]. Nevertheless, basic understanding of the transport phenomena in membraneless co-laminar flow cells is still lacking, especially for the ones employing porous carbon electrodes.

Experimental assessment of the performance of RFBs with different configurations and sizes can be quite cumbersome and expensive. For this reason, a few numerical simulation efforts have been made to simulate flow cells in both membrane-based [24,25] and membraneless [26,27] systems. The availability of versatile discrete numerical methods such as finite elements and finite volumes has enabled the evaluation of the performance of RFBs. On the other hand, analytical methods provide valuable physical insights, low cost solutions to any prescribed accuracy, and benchmark results for the verification of numerical codes. The value of analytically-based methods has been recognized before in the context of RFBs, with a boundary layer analysis of a membraneless hydrogen-bromine flow battery [28,29]. However, analytical methods are usually restricted to linear problems in regular geometries, which severely limits their applicability. With the intent of extending the use of analytical methods beyond these limitations, the so-called hybrid analytical-numerical methods were proposed. Amongst such hybrid methods, the Generalized Integral Transform Technique (GITT) [30–34] is here highlighted. The GITT was shown to be a fairly general technique, being demonstrated in the solution of various classes of diffusion and convection-diffusion problems, such as with moving boundaries, non-linear source terms, heterogeneous media, complex geometries, etc. The main advantages of this method are the automatic error control and mild increase in computational cost with the addition of independent variables. A complete description and broad review of the technique can be found in some compilations published over the years [30–34].

Within the GITT framework, a new strategy for treating problems in heterogeneous media with complex geometries, known as the single domain formulation, has been under development [35–40] and was recently applied to the solution of heterogeneous channel flow governed by the Navier-Stokes equations [41]. Instead of treating the different domains with separate partial differential models coupled through their common boundaries, the single domain formulation proposes a single set of equations in which the coupling between the different media is accomplished through abrupt variations of the physical properties and source terms. The reduced complexity that follows offers far-reaching possibilities for the application of the GITT in classes of problems once mostly dominated by purely numerical approaches.

The present work advances the theoretical analysis and physical understanding of the mass transport phenomena within the scope of membraneless redox flow batteries. A simple case of a cell with flow-by configuration using porous electrodes is analyzed. Both analytical and hybrids solutions to the involved partial differential models for different flow conditions are presented, and critical comparisons are offered. The role of the Reynolds number and the thickness of the electrode on the prevention of crossover is analyzed. The scaling of the dimensionless limiting current density with the Reynolds number and the physical interpretation of this quantity are assessed. Additionally, the dependence of the limiting current with the length of the electrode is examined and some design recommendations are offered.

2. Formulation and solution methodology

2.1. Fluid flow model

Fig. 1 depicts the physical situation involving the hydrodynamic and mass transport simultaneous development along a parallel plate channel partially filled with porous media. A Cartesian coor-