CFD STUDIES ON MASS TRANSPORT IN

REDOX FLOW BATTERIES

BY

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Dedicated to my parents
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LIST OF ABBREVIATIONS

X  X-axis coordinate, mm
Y  Y-axis coordinate, mm
u  X-axis velocity, cm s\(^{-1}\)
\(\langle u \rangle\) average X-axis velocity, cm s\(^{-1}\)
v  Y-axis velocity, cm s\(^{-1}\)
\(\langle v \rangle\) average Y-axis velocity, cm s\(^{-1}\)
p  pressure, kPa
\(\langle p \rangle\) average pressure, kPa
\(\rho\) density, kg m\(^{-3}\)
k  permeability of the porous electrode (or porous layer), m\(^{2}\)
\(k_{\gamma\sigma}\) permeability tensor within \(V_{\gamma\sigma}\), m\(^{2}\)
d  diameter, \(\mu\)m
\(c\) concentration, M
C  constant
\(i\) current density, mA cm\(^{-2}\)
\(a_s\) active surface area of porous material, m\(^{-1}\)
D  diffusivity, cm\(^{2}\) s\(^{-1}\)
stoichiometric coefficient in chemical reactions

Faraday constant, $96,485 \text{ C equiv}^{-1}$

average volume of the representative element of porous solids with neighborhood electrolyte flow, $\mu m^3$

volume of the $\gamma$ phase contained within $V_{\gamma\sigma}, \mu m^3$

volume of the $\sigma$ phase contained within $V_{\gamma\sigma}, \mu m^3$

area of the $\gamma - \sigma$ phase interface contained within $V_{\gamma\sigma}, \mu m^2$

unit normal vector pointing from $\gamma$ phase to $\sigma$ phase, $n_{\gamma\sigma} = -n_{\sigma\gamma}$

point velocity vector for $\gamma$ phase in porous domain, $\text{cm s}^{-1}$

average superficial velocity vector for $\gamma$ phase within $V_{\gamma\sigma}, \text{cm s}^{-1}$

intrinsic average velocity vector for $\gamma$ phase within $V_{\gamma\sigma}, \text{cm s}^{-1}$

fluctuation velocity vector for $\gamma$ phase in the porous domain

$$(\tilde{u}_\gamma = \langle u_\gamma \rangle - u_\gamma), \text{ cm s}^{-1}$$

average superficial pressure for $\gamma$ phase within $V_{\gamma\sigma}, \text{kPa}$

average intrinsic pressure for $\gamma$ phase within $V_{\gamma\sigma}, \text{kPa}$

point pressure for $\gamma$ phase in the porous domain, $\text{kPa}$

fluctuation pressure for $\gamma$ phase in the porous domain

$$(\tilde{p}_\gamma = \langle p_\gamma \rangle - p_\gamma), \text{ kPa}$$
\( \varepsilon_\gamma \)  porosity or volume fraction for \( \gamma \) phase within \( V_{\gamma\sigma} \) (\( \varepsilon_\gamma = V_\gamma/V_{\gamma\sigma} \))

\( \rho_\gamma \)  fluid density for \( \gamma \) phase within \( V_{\gamma\sigma} \), kg m\(^{-3}\)

\( (\rho_\gamma)'^\prime \) intrinsic fluid density for \( \gamma \) phase within \( V_{\gamma\sigma} \), kg m\(^{-3}\)

\( \mu_\gamma \)  dynamic viscosity for \( \gamma \) phase within \( V_{\gamma\sigma} \), Pa\(\cdot\)s

\( \mathbf{g} \)  gravity vector, m s\(^{-2}\)

\( g_x \)  X-axis component of gravity vector, m s\(^{-2}\)

\( g_y \)  Y-axis component of gravity vector, m s\(^{-2}\)

\( \psi \) quantity associated with \( \gamma \) and \( \sigma \) phase in the porous domain

\( t_f \)  thickness of the flow channel, mm (\( t_f = t_{\text{tot}} - t_p \))

\( t_p \)  thickness of the porous layer, mm (\( t_p = t_{\text{tot}} - t_f \))

\( L \) length of the flow channel, mm

**Greek symbols**

\( \Omega \)  domain

\( \Sigma \)  interface

\( \sigma \) solid phase

\( \gamma \) liquid phase

\( \varepsilon \) porosity

\( \ell \) characteristic length in representative porous elements, \( \mu m \)
\( \mu \) dynamic viscosity of the electrolyte fluid, Pa\( \cdot \)s

\( \omega \) volumetric flow rate, ml min\(^{-1}\)

*Subscripts*

\( f \) flow domain

\( p \) porous domain

\( cf \) current collector-flow channel

\( fp \) flow channel-porous layer

\( pm \) porous layer-ion selective membrane

\( pe \) porous element

\( in \) inlet

\( \text{avg} \) average value

\( \text{tot} \) total

\( po \) pore

\( fi \) fiber

\( KC \) Kozeny-Carman

\( \text{max} \) maximum

\( fc \) flow channel

\( pl \) porous layer
Dimensionless number

Re  Reynolds number ($\rho u_{infr} \mu^{-1}$)
A macroscopic model of flow in a redox flow battery is developed. The model is a layered system comprised of a single passage of a serpentine flow channel and a parallel underlying porous electrode (or porous layer). As the fluid moves away from the entrance of the flow channel, two distinct fully developed flow regime evolve in the channel and the underlying porous layer, respectively. The effects of the inlet volumetric flow rates, permeability of the porous layer, thickness of the flow channel and thickness of the porous layer on the nature of the mass flow in the porous layer are investigated. The results show that, for a Reynolds number of 91.5 with the ideal plug flow inlet condition, the average filtration velocity decreases by a factor of about two as the number of carbon fiber paper layers is increased from 1 to 7. Significantly, reactant flow convection is found to estimate a corresponding maximum current density 403 mA cm$^{-2}$ and 742 mA cm$^{-2}$, which compares favorably with experiments of ~400 mA cm$^{-2}$ and ~750 mA cm$^{-2}$, for a single layer and three layers of the carbon fiber paper.
CHAPTER I: Introduction

1.1 Development of Redox Flow Batteries (RFBs)

Redox flow batteries have gained unprecedented attention for energy storage applications. Well-suited for and scalable to utility scale storage, they can be employed to cope with variable or intermittent power generation from renewable energy sources, such as solar and wind energy and are a useful tool for load leveling, peak shaving and emergency back up to improve the stability of the power grid [1,2]. Several research groups are currently working on redox flow batteries. Skyllas-Kazacos et al. [3,4] developed an all-vanadium redox flow battery (all-VRFB) that was motivated by the first study on iron-chrome as a redox couple [5]. An advantage of the all-VRFB is that species crossover leads to only a temporary capacity loss in contrast to a permanent capacity loss for the flow cells with two or more different elements acting as anions or cations in the electrolyte; for example, iron-chromium [6], bromine-polysulfide [7] and zinc-bromine [8], etc. Most recent studies have focused on vanadium flow cells, especially for the all-VRFB. R.F. Savinell et al. [9] developed an all-iron flow cell which has the potential advantage of very low cost. Yet-Ming Chiang et al. [10] designed a semi-solid lithium rechargeable flow battery with using active slurry porous electrode materials through reaction chambers and has shown that improved current density is achieved. M.J. Aziz et al. [11] has introduced an organic & inorganic RFB with quinone reactants in an aqueous electrolyte. High current density and discharge capacity retention have been demonstrated.

Experimental studies on performance and durability for the RFB flow cells are costly and time-consuming. Computational modeling approaches are an effective way to explore
performance improvements without incurring overhead in laboratory time and cost\textsuperscript{[12,13]}. Computational flow battery models developed by Shah et al.\textsuperscript{[13-17]} are dynamic unit cell based approaches\textsuperscript{[13]} that describe isothermal\textsuperscript{[14]}, non-isothermal\textsuperscript{[15]}, hydrogen\textsuperscript{[16]} and oxygen evolution\textsuperscript{[17]} (with bubble formation) in electrochemical transport processes. The models include diffusion, migration and convection and incorporate a dilute-solution approximation method. The numerical results are compared with experiments to be validated with the established models. Vynnycky\textsuperscript{[18]} proposed an asymptotic model combined with a scaling analysis for a large-scale cell stack to save computational time while improving calculation efficiency.

Few experimental and numerical studies on details of flow fields for RFBs have been reported. Kjeang et al.\textsuperscript{[19]} designed a microfluidic vanadium redox fuel cell with a high aspect ratio Y-shaped micro flow channel over a porous carbon substrate to obtain a peak power density of 70mW cm\textsuperscript{2}, which too small for large-scale energy storage applications. Recently, Aaron et al.\textsuperscript{[20,21]}, and Liu\textsuperscript{[22]} et al. designed flow cell stack configurations for RFBs to improve the limiting current density and power density. The objective was to reduce capital costs for commercial energy storage. Specifically, a polarization curve analysis method\textsuperscript{[20]} was used to analyze performance losses in two types of flow cell configurations: (a) a simple battery (SB) with a carbon felt electrode embedded in PVC compartments and (b) a modified direct methanol fuel cell with a serpentine flow channel fuel cell battery (FCB) over the carbon felt (FCB-F) or carbon fiber paper electrode (FCB-P). A higher limiting current density was obtained in the FCB-P than in the SB. A peak power density of 557mW cm\textsuperscript{2}, which is more than five times that obtained using conventional flow cell configurations, was achieved at 60\% state of charge by adopting a
novel “zero-gap” serpentine flow channel fuel cell architecture. Furthermore, superior behavior for lower over-potential was observed in the flow cells composed of two negative porous electrode layers. The potential effects of porous electrodes and ion thermally pretreated selective membranes on the performance of the “zero-gap” serpentine flow cell was also investigated. A peak power density of 767mW cm$^{-2}$ was obtained by using three layers of carbon fiber paper with an oxidative thermal pretreatment and the Nafion 212 membrane. It was proposed out that surface morphologies and oxygen concentrations might alter surface functionalization. It is possible that improvements in the cells performance can be attributed to the thermal treatment for the carbon porous electrodes.

Chen et al. conducted experiments on a parallel flow structure together with CFD analysis for flow distributions in the all-VRFB, but generated a very low power density of 15.9mW cm$^{-2}$. It appears that flow rates may be highly variable over the cell which has motivated calls for an optimized flow field.

Q. Xu et al. made output performance comparisons among different VRFBs with no flow, serpentine and parallel flow channels. The VRFBs with a serpentine flow channel was found to have a higher round trip efficiency. T. Jyothi et al. carried out experiments on a serpentine flow field of RFBs. The effects of rib convection and porous electrode compression on flow distributions and pressure drops were studied. Several comprehensive reviews of RFBs can be found in the literature.

In this thesis, a model is presented that helps explain the maximum current density based on rates of consumption of flow reactants that can be achieved with a single passage of the “zero-gap” serpentine flow battery design.
1.2 “Flow-through” & “Flow-by” RFBs

There are two major porous electrode configurations of RFBs in regard to the directions of the electrolyte flow and current flow: (1) In “flow-through” RFBs, the electrolyte flow is parallel to the current flow as shown in Fig. 1-1 (a) [30] and (b) [30]; (2) in “flow-by” RFBs, the electrolyte flow is perpendicular to the current flow as shown in Fig. 1-2 (a) [30] and (b) [21].

Figure 1-1 Configurations of porous electrodes of “flow-through” RFBs: (a) electrolyte begins to flow at the separator; (b) electrolyte begins to flow at the current collectors
Figure 1-2 Configurations of porous electrodes of “flow-by” RFBs: (a) classic RFBs without flow channels; (b) RFBs with flow channels modified from direct methanol fuel cell (DMFC) or proton exchange membrane fuel cell (PEMFC).

Compared to “flow-by” RFBs, a separator is necessary in the “flow-through” RFBs. These “flow-through” RFBs are sometimes known as “membrane-less” RFBs. However, an ion selective membrane is a requirement in the “flow-by” flow cells. From Fig. 1-1 (a), it can be seen that the electrolyte starts to flow from one edge of the separator, then goes through the porous electrodes and current collectors. At the beginning of cell operations for Fig. 1-
1 (b), the electrolyte starts to move from the current collectors, then goes into the porous electrodes and the separator. Both for Fig. 1-1 (a) and (b), the direction of the electrolyte flow is parallel to the current flow. Another two porous electrode configurations of “flow-by” RFBs are represented in Fig. 1-2 (a) and (b). Fig. 1-2 (a) is the classic “flow-by” flow cell without flow field. This cell design has been widely studied. [12-18] Fig. 1-2 (b) is the “flow-by” flow cell. Here, the flow channels (e.g., serpentine, interdigitated) were originally based on the existing fuel cell technologies, such as direct methanol fuel cell (DMFC), proton exchange membrane fuel cell (PEMFC), etc. The importance of RFB cell with flow field architecture was first suggested by Aaron et al. [21]. They considered electrolyte flowing through the serpentine flow channels.

In a recent review paper, Weber et al. [28] pointed out the conception of “flow-by” and “flow-through” porous electrode structures proposed by Newman et al. [30] can be confusing simply because these terms are also used to describe fluid flow perpendicular to and parallel to the direction of the current flow. Whether or not a flow-by or flow-through porous electrode is used depends on the physical states of the reactants (gas, liquid or solid), the types of chemical reactions and the conductivities of flowing electrolytes. Weber et al. proposed the following: (1)-“flow-through” RFBs as shown in Fig. 1-2 (a) and (2)-“flow-by” RFBs as shown in Fig. 1-2 (b). The flow cell configurations displayed in Fig. 1-1 (a) and (b) were not mentioned. The “flow-by” planar porous electrode architectures of Fig. 1-2 (b) were previously common applications for gaseous reactants flowing in the fuel cell fields.

The definitions of “flow-through” and “flow-by” RFBs proposed by Newman et al. [21,30] will be employed in the modeling and numerical analysis presented in this thesis. Research
on the difference between the “flow-by” and “flow-through” RFBs started in 1970’s. The earliest comparisons between “flow-by” and “flow-through” RFBs were summarized by Newman et al. [30] in 1981. Four kinds of placements of the counter electrodes and the current collectors were discussed: (a) upstream counter electrode, downstream current collector (UD); (b) downstream counter electrode, downstream current collector (DD); (c) upstream counter electrode, upstream current collector (UU) and (d) downstream counter electrode, downstream current collector (DD). Fedkiw [31] found that the “flow-by” RFBs performed better in the limiting current density study. Also, extremely low flow rates in the porous reactor made the “flow-through” RFBs unrealistic [32]. A brief review for discussing advantages and disadvantages for the “flow-through” and “flow-by” porous electrode configurations were given by P.K. Leung et al. [29] and they pointed out that a potential expensive scale-up cost was involved in the “flow-through” RFBs, also the difference between 2D and 3D porous electrodes was illustrated.

Currently, the “flow-by” configuration has been adopted in most of RFBs. Nevertheless, a few studies were still involved in “flow-through” flow cells. Krishnamurthy et al. [33] carried out a numerical analysis of the electrochemical processes in a microfluidic flow cell with a “flow-through” porous electrode. Salloum et al. [34] designed a counter “flow-through” micro flow cell without membrane. The sulfuric acid stream was used to split the electrolyte to prevent diffusive mixing. A vertical microfluidic flow cell configuration with multi-stack of “flow-through” porous electrodes manufactured using a laser ablation and pyrolysis process was proposed by Moore et al. [35]. Kee [36] improved the performance of “flow-through” miniature flow cell by employing a new design and porous electrode material with a less overall loss. Almost all the studies on the “flow-through” porous
electrode configurations are related to microfluidic flow cells (see a review paper by Kjeang et al. [37]). It is possible that micro RFBs are not a good choice for large-scale energy storage applications, because the current density and power density reported by those microfluidic flow cells are very small.
1.3 Motivation

This study analyzes mass transport in a simplified model of redox flow batteries (RFBs) consisting of a single passage of the serpentine flow channel and a porous electrode in parallel. The results obtained by computational fluid dynamics (CFD) are compared with the conventional RFBs without flow channels. Three separate cases are investigated:

(1) Establishing a 2D macroscopic model for describing the primary dynamic motions for the electrolyte flowing through the flow channel and penetrating into the porous electrode. The aim is to capture the coupling mass transport mechanism in the “flow-by” RFBs with a single passage of the serpentine flow channel. Non-dimensional forms of the governing equations and boundary conditions are employed.

(2) Non-dimensional primary flow patterns, entrance lengths and pressure distributions as well as effects from entrance volumetric flow rates, permeability of the porous electrode, thickness of the flow channel and thickness of the porous layer on the mass flow penetration into the porous layer are discussed.

(3) A model for predicting the maximum current density from the reactant convection is proposed and the classic limiting current density models based on the diffusion boundary layer are discussed. Comparisons between the computational results for maximum current density and the experimental results are made.
CHAPTER II: Flow Cell Configurations

A flow battery cell with serpentine flow channels is shown in Fig. 2-1 and this architecture is originally from the work of Aaron et al. [21]. This configuration consists of the following components: 1-end plates; 2-current collectors; 3-graphite plates with the serpentine flow channels; 4-gaskets; 5-porous electrodes; 6-ion selective membrane; 7-load; 8-electrolyte tanks and 9-power pumps. The left and right side of the cell compartment are anode and cathode, respectively. During the discharge process, the anolyte in the tank (8) is circulated by the pump (9) and passes through the serpentine flow channel (3) over the surface of porous electrode (5) and is accompanied by electrochemical reactions. The reactions generate electrons that are conducted via electrical wires to the load. Simultaneously, charge-carrying species are transported through the ion selective membrane. During the charge mode, electrons are absorbed rather than released for anion and cation. The discharge and charge processes are similar in the cathode.
Figure 2-1 The flow cell compartment with serpentine flow channels: 1-end plates; 2-current collectors; 3-graphite plates with serpentine flow channels; 4-gaskets; 5-porous electrodes; 6-ion selective membrane; 7-load; 8-electrolyte tanks and 9-pumps
CHAPTER III: Macroscopic Mathematical Model

A mathematical model is developed to better understand the mass transport mechanism for electrolyte flowing through a single passage of the serpentine flow channel and over the porous electrode. Particular attention is given to the investigation of the flow dynamics within the porous electrode. The Transport Theorem\cite{38-40} and Averaging Volume Method \cite{41} are applied to develop a macroscopic mathematical model, which is largely based on previous studies of Whitaker\cite{39-41}, Gary et al.\cite{42}, Howes et al.\cite{43}, Ochoa-Tapia et al.\cite{44,45}, B. Goyeau et al.\cite{46} and M.L. Bars et al.\cite{47}.

![Flow segments of the serpentine flow channel with the porous electrode in Figure 2-1](image)

The flow passage segments modeled here are shown in Fig. 3-1. The current collector and ion selective membrane bounded by the porous electrode and the serpentine flow channel are not represented in Fig. 3-1. The general components of a single passage of the serpentine flow channel with the porous electrode is shown in Fig. 3-2, which describes a 3D diagram of the electrolyte flowing through the flow channel as a single passage of the serpentine channel and over the porous electrode. A current collector with ion selective membrane are also included.
Figure 3-2 3D diagram of electrolyte flowing through the flow channel and over the porous electrode. Current collector and ion selective membrane as a part of the “flow-by” RFBs with the serpentine flow channels are included.

The flow pattern could be considered as a 2D system with a simplification of the 3D model. The 2D macroscopic model is shown in Fig. 3-3. It illustrates the macroscopic physical structures for the porous electrode, including a representative “average” elements for the porous solids, adjoining electrolyte fluid, and the interface between electrolyte fluid and porous solids. Here, $\Omega_f$ and $\Omega_p$ denote the domain of the flow channel and the porous electrode, respectively. $\Sigma_{cf}$, $\Sigma_{fp}$ and $\Sigma_{pm}$ are the corresponding interfaces between the current collector and the flow channel, the flow channel and the porous electrode and the porous electrode and the ion selective membrane. For each representative element for the porous solids and their neighborhood fluid, $\gamma$ and $\sigma$ denote, respectively, the liquid phase and solid phase and quantities represent a locally average value.
Prior to establishing a macroscopic mathematical model on the fluid through the flow channel $\Omega_f$ and over the porous electrode $\Omega_p$, several formulas and theorems are introduced. An average representative volume porous element for the porous solids and electrolyte fluid is denoted as $V_{y\sigma}$, which contains $\gamma$ phase and $\sigma$ phase for liquid and porous solid, respectively. This volume satisfies

$$V_{y\sigma} = V_\gamma + V_\sigma$$

(3.1)

For any quantity $\psi$, the average value of $\psi$ in the average volume of the representative porous element is expressed in the form

$$\bar{\psi} = \frac{1}{V_{y\sigma}} \int_{V_{y\sigma}} \psi \, dV$$
\[ \langle \psi \rangle = \frac{1}{V_{\gamma \sigma}} \int \psi \, dV \]  

(3.2)

The average quantity \( \psi \) related to \( \gamma \) phase within \( V_{\gamma \sigma} \) can then be represented as

\[ \langle \psi_{\gamma} \rangle = \frac{1}{V_{\gamma}} \int \psi_{\gamma} \, dV \]  

(3.3)

Compared with \( \langle \psi_{\gamma} \rangle \), the average intrinsic phase value \( \langle \psi_{\gamma} \rangle^\gamma \) is defined as

\[ \langle \psi_{\gamma} \rangle^\gamma = \frac{1}{V_{\gamma}} \int \psi_{\gamma} \, dV \]  

(3.4)

Where, the value \( \psi \) in the \( \sigma \) phase is always zero. Through combining formula (3.3) and formula (3.4), the following relationship between \( \langle \psi_{\gamma} \rangle \) and \( \langle \psi_{\gamma} \rangle^\gamma \) is obtained

\[ \langle \psi_{\gamma} \rangle^\gamma = \frac{V_{\gamma \sigma}}{V_{\gamma}} \langle \psi_{\gamma} \rangle \]  

(3.5)

Clearly, \( \langle \psi_{\gamma} \rangle^\gamma \) is always larger than \( \langle \psi_{\gamma} \rangle \), because \( V_{\gamma} \) is always smaller than \( V_{\gamma \sigma} \). The porosity (volume fraction of pore space) for the \( \gamma \) phase is defined as

\[ \varepsilon_{\gamma} = \frac{V_{\gamma}}{V_{\gamma \sigma}} \]  

(3.6)

The formula (3.5) can then be written as

\[ \langle \psi_{\gamma} \rangle = \varepsilon_{\gamma} \langle \psi_{\gamma} \rangle^\gamma \]  

(3.7)
The local point value for $\psi_\gamma$ is related to average intrinsic phase value $<\psi_\gamma>_\gamma$ and the fluctuation phase value $\tilde{\psi}_\gamma$ by $^{[42]}\text{(3.8)}$

$$\psi_\gamma = <\psi_\gamma>_\gamma + \tilde{\psi}_\gamma$$

Since a differential equation with respect to a quantity with time is averaged over the average volume $V_{\gamma\sigma}$, the derivatives of averages are followed. The relationship between averages of derivatives and derivative of averages is given by the Transport Theorem $^{[38-40]}\text{(3.9)}$

$$\langle \frac{\partial \psi_\gamma}{\partial t} \rangle = \frac{\partial <\psi_\gamma>_\gamma}{\partial t} - \frac{1}{V_{\gamma\sigma}} \int \psi_\gamma \mathbf{u}_{\gamma\sigma} \cdot \mathbf{n}_{\gamma\sigma} \, dS$$

Here, $\mathbf{u}_{\gamma\sigma}$ is the velocity vector at the interface between $\gamma$ phase and $\sigma$ phase. The quantity $dS$ denotes the interfacial boundary area between $\gamma$ phase and $\sigma$ phase, $\mathbf{n}_{\gamma\sigma}$ denotes the unit normal vector pointing from $\gamma$ phase to $\sigma$ phase. Similarly, $\mathbf{n}_{\sigma\gamma}$ points from the $\sigma$ phase to the $\gamma$ phase and $\mathbf{n}_{\sigma\gamma}$ is identical to $-\mathbf{n}_{\gamma\sigma}$ as shown in Fig. 3-4.
The “Averaging Theorem” is proposed as \([41]\)

\[
\langle \nabla \psi \rangle = \nabla \langle \psi \rangle + \frac{1}{V_{\gamma\sigma}} \int \psi \mathbf{n}_{\gamma\sigma} \, dS
\]

(3.10)

The formulas and theorems represented in equations (3.1)-(3.10) above provide a theoretical basis to switch from an average value for the derivative of a quantity to the derivative of an average value for a quantity. Those formulas and theorems from related previous studies develop a general framework upon which to build a macroscopic mathematical model that can capture the mass transport mechanism of a single phase flow passing through a flow channel and over the porous electrode. The model for flow over the porous electrode is obtained by averaging mass conservation or continuity and the averaging Navier-Stokes dynamic motions. The major difference between a conventional
flow and flow in the porous medium is that the average value is used to describe the quantities in the latter domain and the integrations over the average volume are needed.
3.1 Averaging mass conservation

The averaging macroscopic mass conservation or continuity equation within the $\gamma$ phase performs a similar form with the continuity equation for the common flow. The electrolyte fluid is assumed to be steady, incompressible, Newtonian and laminar flow. Thus, the continuity equation takes the form

$$\langle \nabla \cdot \mathbf{u}_\gamma \rangle = 0$$  \hspace{1cm} (3.11)

Another identical form for this averaging continuity equation (3.11) is obtained by using “Averaging Theorem” given in formula (3.10)

$$\nabla \cdot \langle \mathbf{u}_\gamma \rangle + \frac{1}{V_{\gamma\sigma}} \int \nabla \cdot \mathbf{u}_\gamma \cdot \mathbf{n}_{\gamma\sigma} dS = 0$$  \hspace{1cm} (3.12)

Providing that a “no slip” boundary condition is adopted for the interface between $\gamma$ phase and $\sigma$ phase and the “no slip” means that the velocity is always zero at the interface, then the averaging continuity equation can be written as

$$\nabla \cdot \langle \mathbf{u}_\gamma \rangle = 0$$  \hspace{1cm} (3.13)

Equation (3.13) is almost identical with the continuity equation for the conventional flow and the only difference is that the velocity in equation (3.13) is an average value.
3.2 Averaging dynamic motion

The averaging dynamic motion in the porous domain is derived by integrating the general momentum motion equation of Navier-Stokes over $V_{\gamma\sigma}$ to obtain an average value for each term as shown in equation (3.14)

\[
\left\langle \frac{\partial (\rho_{\gamma} u_{\gamma})}{\partial t} \right\rangle + \left\langle \nabla \cdot (\rho_{\gamma} u_{\gamma} u_{\gamma}) \right\rangle = -\left\langle \nabla p_{\gamma} \right\rangle + \left\langle \nabla \cdot T \right\rangle + \left\langle \rho_{\gamma} g \right\rangle
\]  

(3.14)

Where, $u_{\gamma}$ is the superficial velocity or filtration velocity vector for $\gamma$ phase, $p_{\gamma}$ is the superficial pressure for $\gamma$ phase, $T$ represents the stress tensor and the formula for $T$ for Newtonian flow is satisfied as below

\[
T = \mu_{\gamma} \left( \nabla u_{\gamma} + (\nabla u_{\gamma})^T \right)
\]  

(3.15)

The first term of equation (3.14) can be written as

\[
\left\langle \frac{\partial (\rho_{\gamma} u_{\gamma})}{\partial t} \right\rangle = \frac{\partial (\rho_{\gamma} u_{\gamma})}{\partial t} - \frac{1}{V_{\gamma\sigma}} \int \rho_{\gamma} u_{\gamma} u_{\gamma\sigma} \cdot n_{\gamma\sigma} dS
\]  

(3.16)

An alternative form for the second term of equation (3.14) is

\[
\left\langle \nabla \cdot (\rho_{\gamma} u_{\gamma} u_{\gamma}) \right\rangle = \nabla \cdot \left( \rho_{\gamma} u_{\gamma} u_{\gamma} \right) + \frac{1}{V_{\gamma\sigma}} \int \rho_{\gamma} u_{\gamma} u_{\gamma} \cdot n_{\gamma\sigma} dS
\]  

(3.17)

Subsequently, the third term of equation (3.14) becomes
\[ \langle \nabla p \rangle = \nabla \langle p \rangle + \frac{1}{V_{\gamma \sigma}} \int p_{\gamma} n_{\gamma \sigma} dS \] (3.18)

The intrinsic phase value forms for pressure and velocity within \( V_{\gamma \sigma} \) are

\[ \langle p_{\gamma} \rangle^\gamma = p_{\gamma} - \hat{p}_{\gamma} \] (3.19)

and

\[ \langle u_{\gamma} \rangle^\gamma = u_{\gamma} - \hat{u}_{\gamma} \] (3.20)

According to formula (3.7), the second term of equation (3.18) becomes

\[ \nabla \langle p \rangle = \nabla (\varepsilon_{\gamma} \langle p \rangle)^\gamma = \varepsilon_{\gamma} \nabla \langle p \rangle^\gamma + \langle p \rangle^\gamma \nabla \varepsilon_{\gamma} \] (3.21)

The third term of equation (3.18) can be written as

\[ \frac{1}{V_{\gamma \sigma}} \int p_{\gamma} n_{\gamma \sigma} dS = \frac{1}{V_{\gamma \sigma}} \int ((p_{\gamma})^\gamma + \hat{p}_{\gamma}) n_{\gamma \sigma} dS = \frac{1}{V_{\gamma \sigma}} \int (p_{\gamma})^\gamma n_{\gamma \sigma} dS + \frac{1}{V_{\gamma \sigma}} \int \hat{p}_{\gamma} n_{\gamma \sigma} dS \] (3.22)

Thus, equation (3.18) can be switched to a modified form

\[ \langle \nabla p \rangle = \varepsilon_{\gamma} \nabla \langle p \rangle^\gamma + \langle p \rangle^\gamma \nabla \varepsilon_{\gamma} + \frac{1}{V_{\gamma \sigma}} \int (p_{\gamma})^\gamma n_{\gamma \sigma} dS + \frac{1}{V_{\gamma \sigma}} \int \hat{p}_{\gamma} n_{\gamma \sigma} dS \] (3.23)

The fourth term of equation (3.14) can be rearranged as
\[
\langle \nabla \cdot \mathbf{T} \rangle = \mu \gamma \langle \nabla^2 \mathbf{u}_\gamma \rangle = \mu \gamma \nabla \cdot \langle \nabla \mathbf{u}_\gamma \rangle + \frac{\mu \gamma}{\nu_{y\sigma}} \int \nabla \mathbf{u}_\gamma \cdot \mathbf{n}_{y\sigma} \, dS \quad (3.24)
\]

Where,

\[
\langle \nabla \mathbf{u}_\gamma \rangle = \nabla \langle \mathbf{u}_\gamma \rangle + \frac{1}{\nu_{y\sigma}} \int \mathbf{u}_\gamma \mathbf{n}_{y\sigma} \, dS \quad (3.25)
\]

By combing equation (3.20) and equation (3.25), equation (3.24) reduces to

\[
\langle \nabla \cdot \mathbf{T} \rangle = \mu \gamma \nabla \langle \nabla^2 \mathbf{u}_\gamma \rangle + \frac{\mu \gamma}{\nu_{y\sigma}} \int \nabla \langle \nabla \mathbf{u}_\gamma \rangle \cdot \mathbf{n}_{y\sigma} \, dS +
\]

\[
\frac{\mu \gamma}{\nu_{y\sigma}} \int \nabla \hat{\mathbf{u}}_\gamma \cdot \mathbf{n}_{y\sigma} \, dS \quad (3.26)
\]

Thus, the following macroscopic model for the dynamic motion transformed from the average Navier-Stokes in the porous domain is obtained

\[
\frac{\partial (\rho \gamma \mathbf{u}_\gamma)}{\partial t} - \frac{1}{\nu_{y\sigma}} \int \rho \gamma \mathbf{u}_\gamma \mathbf{u}_\gamma \cdot \mathbf{n}_{y\sigma} \, dS + \nabla \cdot (\rho \gamma \mathbf{u}_\gamma \mathbf{u}_\gamma) + \frac{1}{\nu_{y\sigma}} \int \rho \gamma \mathbf{u}_\gamma \mathbf{u}_\gamma \cdot \mathbf{n}_{y\sigma} \, dS = -\varepsilon \gamma \nabla \langle p_\gamma \rangle -
\]

\[
\langle p_\gamma \rangle \nabla \varepsilon \gamma - \frac{1}{\nu_{y\sigma}} \int \langle p_\gamma \rangle \mathbf{n}_{y\sigma} \, dS - \frac{1}{\nu_{y\sigma}} \int \mathbf{b}_\gamma \mathbf{n}_{y\sigma} \, dS + \mu \gamma \nabla^2 \langle \mathbf{u}_\gamma \rangle + \mu \gamma \nabla \cdot \left( \frac{1}{\nu_{y\sigma}} \int \mathbf{u}_\gamma \mathbf{n}_{y\sigma} \, dS \right) +
\]

\[
\frac{\mu \gamma}{\nu_{y\sigma}} \int \nabla \langle \mathbf{u}_\gamma \rangle \cdot \mathbf{n}_{y\sigma} \, dS + \frac{\mu \gamma}{\nu_{y\sigma}} \int \nabla \hat{\mathbf{u}}_\gamma \cdot \mathbf{n}_{y\sigma} \, dS + \langle \rho \gamma \mathbf{g} \rangle \quad (3.27)
\]

A “no slip” interfacial boundary condition between fluid and porous solids is assumed, so then the equation (3.27) can be simplified as

36
\[
\frac{\partial(p_\gamma u_\gamma)}{\partial t} + \nabla \cdot (\rho_\gamma u_\gamma u_\gamma) = -\varepsilon_\gamma \nabla(p_\gamma)^\gamma - (p_\gamma)^\gamma \nabla \varepsilon_\gamma - \frac{1}{V_{y\sigma}} \int (p_\gamma)^\gamma n_{y\sigma} \, dS - \frac{1}{V_{y\sigma}} \int \tilde{p}_\gamma n_{y\sigma} \, dS + \\
\mu_\gamma \nabla^2 (u_\gamma) + \frac{\mu_\gamma}{V_{y\sigma}} \int \nabla((u_\gamma)^\gamma) \cdot n_{y\sigma} \, dS + \frac{\mu_\gamma}{V_{y\sigma}} \int \nabla \tilde{u}_\gamma \cdot n_{y\sigma} \, dS + \langle \rho_\gamma g \rangle \quad (3.28)
\]

In order to derive an exact local form, the average intrinsic phase pressure and the average intrinsic phase velocity need to be removed from the area integrations given by the equation (3.28) on the basis of the following length-scale constraints \cite{38-40}

\[
\ell_\gamma \ll r_{pe}, r_{pe}^2 \ll \ell_{\varepsilon_\gamma} \ell_p \quad (3.29)
\]

\[
\ell_\gamma \ll r_{pe}, r_{pe}^2 \ll \ell_{\varepsilon_\gamma} \ell_{u1} \quad (3.30)
\]

Here, \( \ell_{\varepsilon_\gamma} \), \( \ell_p \) and \( \ell_{u1} \) are the characteristic length of porosity, pressure and gradient velocity along X-axis, respectively. The inequality (3.29) is for the average intrinsic phase pressure and the inequality (3.30) is for the average intrinsic phase velocity, then the following equation (3.31) and equation (3.32) are shown

\[
\frac{1}{V_{y\sigma}} \int (p_\gamma)^\gamma n_{y\sigma} \, dS = \langle p_\gamma \rangle^\gamma \frac{1}{V_{y\sigma}} \int n_{y\sigma} \, dS \quad (3.31)
\]

\[
\frac{\mu_\gamma}{V_{y\sigma}} \int \nabla((u_\gamma)^\gamma) \cdot n_{y\sigma} \, dS = \nabla \langle (u_\gamma)^\gamma \rangle \cdot \frac{\mu_\gamma}{V_{y\sigma}} \int n_{y\sigma} \, dS \quad (3.32)
\]

By taking \( \psi = 1 \) in the formula (3.10), equation (3.33) is obtained
\[
\frac{1}{V_{y\sigma}} \int n_{y\sigma} \, dS = -\nabla \varepsilon_y
\]  (3.33)

Equation (3.31) and equation (3.32) reduce to

\[
\frac{1}{V_{y\sigma}} \int \langle p_y \rangle^y n_{y\sigma} \, dS = \langle p_y \rangle^y \frac{1}{V_{y\sigma}} \int n_{y\sigma} \, dS = -\langle p_y \rangle^y \nabla \varepsilon_y
\]  (3.34)

\[
\frac{\mu_y}{V_{y\sigma}} \int \nabla \langle u_y \rangle^y \cdot n_{y\sigma} \, dS = \nabla \langle u_y \rangle^y \cdot \frac{\mu_y}{V_{y\sigma}} \int n_{y\sigma} \, dS = -\mu_y \nabla \langle u_y \rangle^y \cdot \nabla \varepsilon_y
\]  (3.35)

Switching the superficial velocity into the average intrinsic phase velocity, yields

\[
\mu_y \nabla^2 \langle u_y \rangle = \mu_y \nabla \cdot \nabla (\varepsilon_y \langle u_y \rangle^y)
\]  (3.36)

Where,

\[
\nabla (\varepsilon_y \langle u_y \rangle^y) = \varepsilon_y \nabla \langle u_y \rangle^y + \langle u_y \rangle^y \nabla \varepsilon_y
\]  (3.37)

Applying the index notation method, equation (3.37) is transformed as follows

\[
\nabla \cdot \nabla (\varepsilon_y \langle u_y \rangle^y) = \frac{\partial (\varepsilon_y \langle u_y \rangle^y)}{\partial x^l} + \frac{\partial \langle u_y \rangle^y \varepsilon_y}{\partial x^l} = \varepsilon_y \frac{\partial \langle u_y \rangle^y}{\partial x^l} + (\nabla \langle u_y \rangle^y) \frac{\partial \varepsilon_y}{\partial x^l} + \langle u_y \rangle^y \frac{\partial \varepsilon_y}{\partial x^l} + (\nabla \varepsilon_y) \frac{\partial \langle u_y \rangle^y}{\partial x^l}
\]

(3.38)

The index notation terms of the equation (3.38) are
Here, a simplifying form of equation (3.28) is derived from the combinations of equation (3.34), equation (3.35) and equation (3.39) with regarding a very small variation of porosity for the $\gamma$ phase within $V_{\gamma\sigma}$

$$\frac{\partial(p_\gamma u_\gamma)}{\partial t} + \nabla \cdot (p_\gamma u_\gamma u_\gamma) = -\varepsilon_\gamma \nabla (p_\gamma)^\gamma - \frac{1}{V_{\gamma\sigma}} \int \rho_\gamma n_{\gamma\sigma} dS + \mu_\gamma (\varepsilon_\gamma \cdot \nabla^2 (u_\gamma)^\gamma + (u_\gamma)^\gamma \cdot \nabla^2 \varepsilon_\gamma + \nabla \varepsilon_\gamma \cdot (u_\gamma)^\gamma) + \frac{1}{V_{\gamma\sigma}} \int (\mu_\gamma \nabla \hat{u}_\gamma - I \hat{p}_\gamma) \cdot n_{\gamma\sigma} dS + (\rho_\gamma g)$$

(3.41)

According to the reference \cite{42} 

$$\langle \rho_\gamma u_\gamma \rangle = \varepsilon_\gamma \langle \rho_\gamma \rangle^\gamma (u_\gamma)^\gamma + \langle \hat{p}_\gamma \hat{u}_\gamma \rangle$$

(3.42)

$$\langle \rho_\gamma u_\gamma u_\gamma \rangle = \varepsilon_\gamma \langle \rho_\gamma \rangle^\gamma (u_\gamma)^\gamma \cdot (u_\gamma)^\gamma + \langle \rho_\gamma \rangle^\gamma (\hat{u}_\gamma \hat{u}_\gamma) + 2 (u_\gamma)^\gamma (\hat{p}_\gamma \hat{u}_\gamma) + \langle \hat{p}_\gamma \hat{u}_\gamma \hat{u}_\gamma \rangle$$

(3.43)
The expansions of the first term of the equation (3.41) are obtained by using equation (3.42)

\[
\frac{\partial (\rho \gamma u_\gamma)}{\partial t} = (\rho_\gamma)^Y (u_\gamma)^Y \frac{\partial \varepsilon_\gamma}{\partial t} + \varepsilon_\gamma (u_\gamma)^Y \frac{\partial (\rho_\gamma)^Y}{\partial t} + \varepsilon_\gamma (\rho_\gamma)^Y \frac{\partial (u_\gamma)^Y}{\partial t} + \frac{\partial (\hat{\rho}_\gamma \hat{u}_\gamma)}{\partial t}
\]  (3.44)

Also,

\[
\nabla \cdot (\rho_\gamma u_\gamma u_\gamma) = \nabla \cdot ((\rho_\gamma)^Y (u_\gamma)^Y) + 2 \nabla \cdot ((u_\gamma)^Y (\hat{u}_\gamma \hat{u}_\gamma)) + \nabla \cdot ((\hat{\rho}_\gamma \hat{u}_\gamma))
\]  (3.45)

Therefore, equation (3.41) reduces to

\[
(\rho_\gamma)^Y (u_\gamma)^Y \frac{\partial \varepsilon_\gamma}{\partial t} + \varepsilon_\gamma (u_\gamma)^Y \frac{\partial (\rho_\gamma)^Y}{\partial t} + \varepsilon_\gamma (\rho_\gamma)^Y \frac{\partial (u_\gamma)^Y}{\partial t} + \frac{\partial (\hat{\rho}_\gamma \hat{u}_\gamma)}{\partial t} + \nabla \cdot ((\rho_\gamma)^Y (u_\gamma)^Y) + \nabla \cdot ((u_\gamma)^Y (\hat{u}_\gamma \hat{u}_\gamma)) + \nabla \cdot ((\hat{\rho}_\gamma \hat{u}_\gamma)) = -\varepsilon_\gamma \nabla (\rho_\gamma)^Y + \mu_\gamma (\varepsilon_\gamma \cdot

\nabla^2 (u_\gamma)^Y + (u_\gamma)^Y \cdot \nabla^2 \varepsilon_\gamma + \nabla \varepsilon_\gamma \nabla \cdot (u_\gamma)^Y) + \frac{1}{\nu_\gamma} \int (\mu_\gamma \nabla \hat{u}_\gamma - I \hat{p}_\gamma) \cdot n_\gamma dS + (\rho_\gamma g)
\]  (3.46)

Equation (3.46) expresses a general form of the 2D macroscopic model for fluid flowing through the homogenous porous medium, and the “no-slip” boundary condition between fluid and porous solids is employed based on an assumption that the porous solids are stationary. The flow is regarded as steady, and the terms related to time are negligible. Thus, a simplified form for the equation (3.46) is
\[ \nabla \cdot (\varepsilon_{\gamma}(\rho_{\gamma})^Yu_{\gamma}^Y(u_{\gamma})^Y) + \nabla \cdot ((\rho_{\gamma})^Y(\hat{u}_{\gamma}\hat{u}_{\gamma})) + 2\nabla \cdot (u_{\gamma})^Y(\hat{u}_{\gamma}\hat{u}_{\gamma}) + \nabla \cdot (\hat{\rho}_{\gamma}\hat{u}_{\gamma}\hat{u}_{\gamma}) = \\
-\varepsilon_{\gamma}\nabla (\rho_{\gamma})^Y + \mu_{\gamma}(\varepsilon_{\gamma} \cdot \nabla^2 (u_{\gamma})^Y + \langle u_{\gamma} \rangle^Y \cdot \nabla \varepsilon_{\gamma} + \nabla \varepsilon_{\gamma} \cdot \langle u_{\gamma} \rangle^Y) + \frac{\mu_{\gamma}}{\nu_{\gamma}} \int (\nabla \hat{u}_{\gamma} - I \hat{\rho}_{\gamma}) \cdot \\
n_{\gamma} \delta > (\rho_{\gamma} g) \] (3.47)

The magnitude of terms involved in the equation (3.47) is determined through the length-scale constraints applied with the following scaling terms

\[ \nabla \cdot (\varepsilon_{\gamma}(\rho_{\gamma})^Y(u_{\gamma})^Y): O\left(\frac{\varepsilon_{\gamma}(\rho_{\gamma})^Y(u_{\gamma})^Y}{\varepsilon_{1}}\right) \] (3.48)

\[ \nabla \cdot ((\rho_{\gamma})^Y(\hat{u}_{\gamma}\hat{u}_{\gamma})): O\left(\frac{(\rho_{\gamma})^Y(\hat{u}_{\gamma}\hat{u}_{\gamma})}{\varepsilon_{2}}\right) \] (3.49)

\[ \nabla \cdot (u_{\gamma})^Y(\hat{u}_{\gamma}\hat{u}_{\gamma}): O\left(\frac{(u_{\gamma})^Y(\hat{u}_{\gamma}\hat{u}_{\gamma})}{\varepsilon_{3}}\right) \] (3.50)

\[ \nabla \cdot (\hat{\rho}_{\gamma}\hat{u}_{\gamma}\hat{u}_{\gamma}): O\left(\frac{(\hat{\rho}_{\gamma}\hat{u}_{\gamma}\hat{u}_{\gamma})}{\varepsilon_{4}}\right) \] (3.51)

\[ \varepsilon_{\gamma}\nabla (\rho_{\gamma})^Y: O\left(\frac{\varepsilon_{\gamma}(\rho_{\gamma})^Y}{\varepsilon_{p1}}\right) \] (3.52)

\[ \mu_{\gamma}\varepsilon_{\gamma} \cdot \nabla^2 (u_{\gamma})^Y: O\left(\frac{\mu_{\gamma}\varepsilon_{\gamma}(u_{\gamma})^Y}{\varepsilon_{u2}}\right) \] (3.53)

\[ \mu_{\gamma}\nabla^2 (u_{\gamma})^Y \cdot \nabla^2 \varepsilon_{\gamma}: O\left(\frac{\mu_{\gamma}(u_{\gamma})^Y\varepsilon_{\gamma}}{\varepsilon_{u2}\varepsilon_{\gamma}}\right) \] (3.54)
\[ \mu_y \nabla \varepsilon_y \nabla \cdot (\mathbf{u}_y)^\gamma \cdot \mathbf{O}\left(\frac{\mu_y \varepsilon_y (\mathbf{u}_y)^\gamma}{\ell_{u1}}\right) \quad (3.55) \]

\[ \frac{1}{V_y} \int \mu_y \nabla \tilde{\mathbf{u}}_y \cdot \mathbf{n}_{y\sigma} \; dS: \mathbf{O}\left(\frac{\mu_y (\mathbf{u}_y)^\gamma}{\ell_{u1}}\right) \quad (3.56) \]

\[ \frac{1}{V_y} \int -\mathbf{f}_\gamma \cdot \mathbf{n}_{y\sigma} \; dS: \mathbf{O}\left(\frac{\mu_y (p_y)^\gamma}{\ell_{p1}}\right) \quad (3.57) \]

Where, \( \ell_1, \ell_2, \ell_3, \ell_4 \) and \( \ell_{p1} \) is the characteristic length of the first order derivative of \( \varepsilon_y (\rho_y)^\gamma (\mathbf{u}_y)^\gamma, (\rho_y)^\gamma (\mathbf{u}_y)^\gamma (\mathbf{u}_y), (\mathbf{u}_y)^\gamma (\mathbf{u}_y), (\mathbf{u}_y)^\gamma (\mathbf{u}_y), \) and \( (p_y)^\gamma, \) respectively. \( \ell_{\varepsilon1} \) and \( \ell_{u1} \) are respectively, the corresponding characteristic length of the first order derivative of porosity and velocity. \( \ell_{\varepsilon2} \) and \( \ell_{u2} \) are the characteristic length of the second derivative of porosity and velocity, respectively. It is a challenge to determine the characteristic scale lengths \( \ell_1, \ell_2, \ell_3, \ell_4, \ell_{p1}, \ell_{u1}, \ell_{\varepsilon1}, \ell_{\varepsilon2} \) and \( \ell_{u2} \). In past work \(^{39-41}\) and in Whitaker et al., it is argued that terms in (3.48), (3.49), (3.50) and (3.51) are much smaller than terms on the right side of equation (3.47) and the variations of \( \varepsilon_y \) are negligible. Furthermore, the terms of (3.52), (3.56) and (3.57) are believed to be more important \(^{39-41}\) than the terms of (3.53), (3.54) and (3.55). Under these assumptions, a simplified form of the equation (3.47) is obtained

\[ 0 = -\varepsilon_y \nabla (p_y)^\gamma + \frac{1}{V_y} \int (\mu_y \nabla \tilde{\mathbf{u}}_y - \mathbf{f}_\gamma) \cdot \mathbf{n}_{y\sigma} \; dS + (\rho_y \mathbf{g}) \quad (3.58) \]

However, in the equation (3.58), the term \( \mu_y \varepsilon_y \nabla^2 (\mathbf{u}_y)^\gamma \) (known as the Brinkman term) was neglected. According to H.C. Brinkman \(^{48}\), Ochoa-Tapia et al. \(^{44,45}\), \( \mu_y \varepsilon_y \nabla^2 (\mathbf{u}_y)^\gamma \) the
Brinkman term is potentially important, so a modified form for equation (3.58) is obtained as

\[
0 = -\varepsilon_y \nabla (p_y)^Y + \mu_y \varepsilon_y \nabla^2 (u_y)^Y + \frac{1}{V_{\gamma \sigma}} \int (\mu_y \nabla \hat{u}_y - \hat{I} \hat{p}_y) \cdot n_{\gamma \sigma} \, dS + \langle \rho_y g \rangle \tag{3.59}
\]

A more clear explicit expression for \( \frac{1}{V_{\gamma \sigma}} \int (\mu_y \nabla \hat{u}_y - \hat{I} \hat{p}_y) \cdot n_{\gamma \sigma} \, dS \) is [38-40]

\[
\frac{1}{V_{\gamma \sigma}} \int (\mu_y \nabla \hat{u}_y - \hat{I} \hat{p}_y) \cdot n_{\gamma \sigma} \, dS = -\mu_y k_{\gamma \sigma}^{-1} (u_y)^Y \tag{3.60}
\]

Here, \( k_{\gamma \sigma} \) is the permeability tensor. By taking equation (3.60) and Brinkman’s term into consideration and the length scale constraints from Whitaker et al. are adopted in this model, equation (3.47) becomes

\[
0 = -\varepsilon_y \nabla (p_y)^Y + \mu_y \varepsilon_y \cdot \nabla^2 (u_y)^Y - \mu_y k_{\gamma \sigma}^{-1} (u_y)^Y + \langle \rho_y g \rangle \tag{3.61}
\]

Here, the fluctuation velocity and pressure is considered far smaller than the average phase intrinsic velocity and the average intrinsic pressure. The superficial velocity is used, then equation (3.61) is modified as

\[
0 = -\varepsilon_y \nabla (p_y)^Y + \mu_y \nabla^2 (u_y) - \mu_y \varepsilon_y k_{\gamma \sigma}^{-1} (u_y) + \langle \rho_y g \rangle \tag{3.62}
\]

Where, \( \langle \rho_y g \rangle = \varepsilon_y \rho_y g \)
It’s interesting to see that if the viscous force term is negligible as Whitaker mentioned

\[ \mu_y \nabla^2 (u_y) \sim O(0) \quad (3.63) \]

If gravity is neglected, equation (3.62) can be further simplified to

\[ \langle u_y \rangle = -\frac{k_{\gamma\sigma}}{\mu_y} \nabla (p_\gamma)' \quad (3.64) \]

This formula (3.64) is the well-known Darcy’s law, which states that the superficial velocity is proportional to the permeability of the porous medium and the gradient of the pressure exerted on the flow but inversely proportional to the dynamic viscosity of fluid. It is easy to infer that Darcy’s law deals with the flow patterns without regarding the viscous force term (Brinkman term). However, the viscous force will be taken into consideration in this macroscopic mathematical model used here. Equation (3.62) is the model for the dynamic motion in the porous electrode and this model incorporates Darcy’s law and Brinkman’s term. Thus, equation (3.62) is named as Brinkman-Darcy model. Steady, incompressible, laminar Navier-Stokes flow is assumed in the flow channel

\[ \rho u \cdot \nabla u = -\nabla p + \mu \nabla^2 u + \rho g \quad (3.65) \]

Here, \( u \) is velocity vector, and \( \mu \) is the dynamic viscosity of fluid. Later in this work, \( \varepsilon_\gamma, \mu_\gamma, k_{\gamma\sigma}, \langle p_\gamma \rangle' \) and \( \langle u_\gamma \rangle \) in the equation (3.62) will be replaced by \( \varepsilon, \mu, k, \langle p \rangle, \langle u_p \rangle \) and \( \langle v_p \rangle \) in the porous domain and \( p, u_f \) and \( v_f \) will be used in equation (3.65) for the flow channel.
### 3.3 Boundary conditions

7 non-dimensional boundary conditions are determined: BC#1, BC#2, BC#3, BC#4, BC#5, BC#6, and BC#7 described in Fig. 3-3 and Table 1. The BC#1 is assumed to be the ideal plug flow inlet rather than the ideal parabolic flow inlet and the reason is that the entrance electrolyte flow is from a perpendicularly oriented feeder pipe and this entrance flow is more likely to be uniform. The determination of BC#4 as the interface boundary condition between the flow channel and the porous layer is the most challenging. The earliest work on the boundary condition between the flow channel and the porous medium was proposed by Beavers and Joseph [49] in 1967, a semi-empirical slip boundary was proposed as Poiseuille fluid flowing over the permeable wall. They pointed out that a possible boundary layer should exist around the interface and the theoretical slip coefficient $\alpha$ had a reasonable agreement with their experiments for using demineralized water and oil through the upper parallel plate and the lower porous material (four kinds of foametal and two kinds of aloxite) system formed with the upper impermeable wall and the lower semi-infinite permeable block by fitting the value of $\alpha$ from 0.1 to 4. However, the value of $\alpha$ was hard to be determined for practical porous material as not homogenous and isotropic. In 1971, P.G. Saffman [50] made a modification for Beavers and Joseph’s condition and the filtration velocity was in the same order magnitude of the square root of the porous medium’s permeability. Obviously, when the permeability is very small, then the filtration velocity could be negligible compared with fluid velocity in the flow channel. Further studies followed by Neal and Nader [51], Williams [52], Ochoa-Tapia and Whitaker [44,45], Vafai [53-55], Kim [56], Kazmierczak [57] and Chandesris [58,59] and others. Whether the stress jump and continuity of velocity exists at the interface are the major questions. A non-
physical effective viscosity \((\mu_{\text{eff}} = \mu/\varepsilon)\) has been proposed. In this model, a common interfacial boundary condition for BC#4 is adopted that accounts for the continuity of velocity and normal stress \([55-57,60,61]\). Informative review papers on BC#4 are found in references \([61,62]\). Moreover, the BC#7 as the interface between the porous layer and the ion selective membrane is considered as “no slip”, which states that the velocity at BC#7 is zero and it’s based the stationary ion selective membrane.

Table 1 Boundary conditions: BC#1, BC#2, BC#3, BC#4, BC#5, BC#6 and BC#7

<table>
<thead>
<tr>
<th>Type</th>
<th>Coordinates</th>
<th>Boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>(X = 0, 0 \leq Y \leq t_f)</td>
<td>(u_t = u_{\text{in}})  (v_t = 0)</td>
</tr>
<tr>
<td>#2</td>
<td>(0 &lt; X &lt; L, Y = t_f)</td>
<td>(u_t = 0)  (v_t = 0)</td>
</tr>
<tr>
<td>#3</td>
<td>(X = L, 0 \leq Y \leq t_f)</td>
<td>(p_t = 0)  (v_t = 0)</td>
</tr>
<tr>
<td>#4</td>
<td>(0 &lt; X &lt; L, Y = 0)</td>
<td>(u_t(\Sigma_{pt}) = \langle u_p(\Sigma_{pt}) \rangle)  (v_t(\Sigma_{pt}) = \langle v_p(\Sigma_{pt}) \rangle)  (p_t(\Sigma_{pt}) = \langle p_p(\Sigma_{pt}) \rangle)  (\frac{\partial u_t}{\partial Y}(\Sigma_{pt}) = \frac{1}{\varepsilon} \frac{\partial (u_p(\Sigma_{pt}))}{\partial Y})</td>
</tr>
<tr>
<td>#5</td>
<td>(X = 0, -t_p &lt; Y &lt; 0)</td>
<td>(u_t = 0)  (v_t = 0)</td>
</tr>
<tr>
<td>#6</td>
<td>(X = L, -t_p &lt; Y &lt; 0)</td>
<td>(u_t = 0)  (v_t = 0)</td>
</tr>
</tbody>
</table>
| #7 | \(0 \leq X \leq L, Y = -t_p\) | \(u_f = 0\)  \\
|    |                             | \(v_f = 0\) |
3.4 Non-dimensionalization

Based on the assumptions mentioned above: steady, incompressible, Newtonian and laminar flow, the non-dimensional forms for fluid dynamics in the flow channel $\Omega_f$ and the porous layer $\Omega_p$ are derived as follows. The normalized forms include the continuity equation and equations of motion. The non-dimensional parameters are defined in Table 2.

Table 2 Non-dimensional parameters

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Definitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^*$</td>
<td>$X/L$</td>
</tr>
<tr>
<td>$Y^*$</td>
<td>$Y/(t_p+t_f)$</td>
</tr>
<tr>
<td>$u_i^*$</td>
<td>$u_i/u_{in}$</td>
</tr>
<tr>
<td>$v_i^*$</td>
<td>$v_i/u_{in}$</td>
</tr>
<tr>
<td>$\langle u_p \rangle^*$</td>
<td>$\langle u_p \rangle/u_{in}$</td>
</tr>
<tr>
<td>$\langle v_p \rangle^*$</td>
<td>$\langle v_p \rangle/u_{in}$</td>
</tr>
<tr>
<td>$p_i^*$</td>
<td>$p_i/\rho u_{in}^2$</td>
</tr>
<tr>
<td>$\langle p_p \rangle^*$</td>
<td>$\langle p_p \rangle/\rho u_{in}^2$</td>
</tr>
<tr>
<td>$Re$</td>
<td>$\rho u_{in} t_f/\mu$</td>
</tr>
</tbody>
</table>
3.4.1 Flow channel

The continuity equation and Navier-Stokes equations for a Newtonian fluid are applied to describe the flow regime in the flow channel.

\[ \nabla \cdot \mathbf{u}_f = 0 \]  \hspace{1cm} (3.66)

Equation (3.66) is normalized as below

\[ \frac{\partial (u_f^*u_{in})}{\partial (X^*L)} + \frac{\partial (v_f^*u_{in})}{\partial (Y^*(t_f+t_p))} = 0 \]  \hspace{1cm} (3.67)

Making a rearrangement

\[ \frac{\partial u_f^*}{\partial X^*} + \frac{L}{(t_f+t_p)} \frac{\partial v_f^*}{\partial Y^*} = 0 \]  \hspace{1cm} (3.68)

The Navier-Stokes motions along the X-axis are, in non-dimensional form

\[ \rho u_f^* \cdot u_{in} \frac{\partial (u_f^*u_{in})}{\partial (X^*L)} + \rho v_f^* \cdot u_{in} \frac{\partial (u_f^*u_{in})}{\partial (Y^*(t_f+t_p))} = -\frac{\partial (p_f^*\rho u_{in}^2)}{\partial (X^*L)} + \mu \left( \frac{\partial}{\partial (X^*L)} \left( \frac{\partial (u_f^*u_{in})}{\partial (X^*L)} \right) \right) + \mu \left( \frac{\partial}{\partial (Y^*(t_f+t_p))} \left( \frac{\partial (u_f^*u_{in})}{\partial (Y^*(t_f+t_p))} \right) \right) \]  \hspace{1cm} (3.69)

or, alternatively,
\[ \frac{\rho u_{in}^2}{L} u_f^* \frac{\partial u_f^*}{\partial x^*} + \frac{\rho u_{in}^2}{(t_f+t_p)} v_f^* \frac{\partial u_f^*}{\partial y^*} = -\frac{\rho u_{in}^2}{L} \frac{\partial p_{f}^*}{\partial x^*} + \frac{\mu u_{in}}{L^2} \frac{\partial^2 u_f^*}{\partial x^*^2} + \frac{\mu u_{in}}{(t_f+t_p)^2} \frac{\partial^2 u_f^*}{\partial y^*^2} \]  

(3.70)

Divided by \( \frac{\mu u_{in}}{(t_f+t_p)^2} \), equation (3.70) becomes

\[ \frac{\rho u_{in}t_f(t_f+t_p)^2}{\mu t_f L} u_f^* \frac{\partial u_f^*}{\partial x^*} + \frac{\rho u_{in}t_f(t_f+t_p)}{t_f} v_f^* \frac{\partial u_f^*}{\partial y^*} = -\frac{\rho u_{in}t_f(t_f+t_p)^2}{\mu t_f L} \frac{\partial p_{f}^*}{\partial x^*} + \frac{(t_f+t_p)^2}{L^2} \frac{\partial^2 u_f^*}{\partial x^*^2} + \frac{\partial^2 u_f^*}{\partial y^*^2} \]  

(3.71)

If \( \frac{\rho u_{in}t_f}{\mu} \) is replaced with Re (Reynolds number), then equation (3.71) becomes

\[ \text{Re} \frac{(t_f+t_p)^2}{t_f L} u_f^* \frac{\partial u_f^*}{\partial x^*} + \text{Re} \frac{(t_f+t_p)}{t_f} v_f^* \frac{\partial u_f^*}{\partial y^*} = -\text{Re} \frac{(t_f+t_p)^2}{t_f L} \frac{\partial p_{f}^*}{\partial x^*} + \frac{(t_f+t_p)^2}{L^2} \frac{\partial^2 u_f^*}{\partial x^*^2} + \frac{\partial^2 u_f^*}{\partial y^*^2} \]  

(3.72)

Similarly, Navier-Stokes motion along Y-axis is normalized as

\[ \rho u_f^* \cdot u_{in} \frac{\partial (v_f^* - u_{in})}{\partial (X \cdot L)} + \rho v_f^* \cdot u_{in} \frac{\partial (v_f^* - u_{in})}{\partial (Y^* \cdot (t_f+t_p))} = -\rho g \left( \frac{\partial (v_f^* - u_{in})}{\partial (X \cdot L)} + \mu \left( \frac{\partial}{\partial (Y^* \cdot (t_f+t_p))} \left( \frac{\partial (v_f^* - u_{in})}{\partial (X \cdot L)} \right) \right) \right) + \mu \left( \frac{\partial}{\partial (Y^* \cdot (t_f+t_p))} \left( \frac{\partial (v_f^* - u_{in})}{\partial (X \cdot L)} \right) \right) \]  

(3.73)

Rearranging equation (3.73)

\[ \frac{\rho u_{in}^2}{L} u_f^* \frac{\partial v_f^*}{\partial x^*} + \frac{\rho u_{in}^2}{(t_f+t_p)} v_f^* \frac{\partial v_f^*}{\partial y^*} = -\frac{\rho u_{in}^2}{(t_f+t_p)} \frac{\partial p_{f}^*}{\partial y^*} + \frac{\mu u_{in}}{L^2} \frac{\partial^2 v_f^*}{\partial x^*^2} + \frac{\mu u_{in}}{(t_f+t_p)^2} \frac{\partial^2 v_f^*}{\partial y^*^2} - \rho g \]  

(3.74)
Divided by \( \frac{\mu_{in}}{(t_f+t_p)^2} \), equation (3.74) becomes

\[
\text{Re} \left( \frac{t_f+2}{t_f} \right) u_f^* \frac{\partial v_f^*}{\partial x^*} + \text{Re} \left( \frac{t_f+2}{t_f} \right) v_f^* \frac{\partial v_f^*}{\partial y^*} = -\text{Re} \left( \frac{t_f+t_p}{L} \right) \frac{\partial p_f^*}{\partial y^*} + \frac{(t_f+t_p)^2}{L^2} \frac{\partial v_f^*}{\partial x^*} + \frac{\partial v_f^*}{\partial y^*} - \frac{\rho g (t_f+t_p)^2}{\mu_{in}}
\]

(3.75)

Thus, equation (3.68) represents continuity, and equation (3.72) and equation (3.75) are the dimensionless Navier-Stokes equations along the X-axis and Y-axis, respectively.
3.4.2 Porous layer

The averaging mass conservation equation (3.13) and dynamic motion equation (3.62) in the porous layer are normalized below

\[ \frac{\partial ((u_p)\cdot u_{in})}{\partial (X') \cdot L} + \frac{\partial ((v_p)\cdot u_{in})}{\partial (Y' \cdot (t_f + t_p))} = 0 \]  

(3.76)

Simplifying equation (3.76)

\[ \frac{\partial ((u_p)^*)}{\partial (X^*)} + \frac{L}{(t_f + t_p)} \frac{\partial ((v_p)^*)}{\partial (Y^*)} = 0 \]  

(3.77)

The dimensionless form of the dynamic motion in X-axis of equation (3.62) is derived as

\[ -\varepsilon \frac{\partial ((p_p)^* \cdot u_{in}^2)}{\partial (X')} + \mu \left( \frac{\partial ((u_p)^* \cdot u_{in})}{\partial (X')} \right) + \frac{\mu u_{in}}{L^2} \left( \frac{\partial ((u_p)^*)}{\partial (X')} \right) + \mu \frac{u_{in}}{(t_f + t_p)} \left( \frac{\partial ((u_p)^*)}{\partial (Y')} \right) - \mu \varepsilon k^{-1} (u_p)^* \cdot u_{in} = 0 \]  

(3.78)

Rearranging equation (3.78)

\[ -\varepsilon \frac{\rho u_{in}^2 \partial ((p_p)^*)}{L \partial (X')} + \frac{\mu u_{in}}{L^2} \left( \frac{\partial ((u_p)^*)}{\partial (X')} \right) + \frac{\mu u_{in}}{(t_f + t_p)} \left( \frac{\partial ((u_p)^*)}{\partial (Y')} \right) - \mu \varepsilon k^{-1} (u_p)^* \cdot u_{in} = 0 \]  

(3.79)

Divided by \(\mu u_{in}\) and terms with Re is substituted, then equation (3.79) reduces to
\[-\varepsilon \text{Re} \frac{\partial ((p_p)^*)}{\partial (X^*)} + \frac{1}{L^2} \frac{\partial^2 ((u_p)^*)}{\partial (X^*)^2} + \frac{1}{(t_f + t_p)^2} \frac{\partial^2 ((u_p)^*)}{\partial (Y^*)^2} - \frac{\varepsilon}{k} (u_p)^* = 0 \]  \hspace{1cm} (3.80)

The normalized dynamic motion of equation (3.62) in Y-axis is derived

\[-\varepsilon \frac{\partial ((p_p)^* \cdot \rho u_{in}^2)}{\partial (Y^* (t_f + t_p))} + \mu \left( \frac{\partial}{\partial (X^* L)} \left( \frac{\partial ((v_p)^* \cdot \rho u_{in})}{\partial (X^* L)} \right) \right) + \mu \left( \frac{\partial}{\partial (Y^* (t_f + t_p))} \left( \frac{\partial ((v_p)^* \cdot \rho u_{in})}{\partial (Y^* (t_f + t_p))} \right) \right) - \mu \varepsilon k^{-1} (v_p)^* \cdot \]

\[u_{in} - \varepsilon \rho g = 0 \]  \hspace{1cm} (3.81)

Simplifying equation (3.81)

\[-\varepsilon \text{Re} \frac{\partial ((p_p)^*)}{\partial (Y^*)} + \frac{1}{L^2} \frac{\partial^2 ((v_p)^*)}{\partial (X^*)^2} + \frac{1}{(t_f + t_p)^2} \frac{\partial^2 ((v_p)^*)}{\partial (Y^*)^2} - \frac{\varepsilon}{k} (v_p)^* - \frac{\rho g \varepsilon}{\mu u_{in}} = 0 \]  \hspace{1cm} (3.82)

Equation (3.77), equation (3.80) and equation (3.82) are the dimensionless forms for the averaging mass conservation, averaging flow dynamic motions in X-axis and Y-axis, respectively. The non-dimensional boundary conditions are determined through using the normalized symbols mentioned in Table 2:

(1) BC\#1-inlet of the flow channel

\[X^* = 0, 0 \leq Y^* \leq \frac{t_f}{t_f + t_p}, u_f^* = 1, v_f^* = 0 \]  \hspace{1cm} (3.83)
(2) BC#2-upper wall of the flow channel

\[ 0 < X^* < 1, \ Y^* = \frac{t_f}{t_f + t_p}, \ u_f^* = 0, \ v_f^* = 0 \]  

(3.84)

(3) BC#3-outlet of the flow channel

\[ X^* = 1, \ 0 \leq Y^* \leq \frac{t_f}{t_f + t_p}, \ p_f^* = 0, \ v_f^* = 0 \]  

(3.85)

(4) BC#4-interface between the flow channel and the porous layer

\[ 0 < X^* < 1, \ Y^* = 0, \ u_f^* (\Sigma_f) = \langle u_p \rangle (\Sigma_p) \]  

(3.86)

\[ 0 < X^* < 1, \ Y^* = 0, \ v_f^* (\Sigma_f) = \langle v_p \rangle (\Sigma_p) \]  

(3.87)

\[ 0 < X^* < 1, \ Y^* = 0, \ p_f^* (\Sigma_f) = \langle p_p \rangle (\Sigma_p) \]  

(3.88)

\[ 0 < X^* < 1, \ Y^* = 0, \ \frac{\partial u_f^*}{\partial Y^*} (\Sigma_f) = \frac{1}{\varepsilon} \frac{\partial \langle u_p \rangle}{\partial Y^*} (\Sigma_p) \]  

(3.89)

(5) BC#5-left side wall of the porous layer

\[ X^* = 0, \ -\frac{t_p}{t_f + t_p} < Y^* < 0, \ \langle u_p \rangle^* = 0, \ \langle v_p \rangle^* = 0 \]  

(3.90)
(6) BC#6-right side wall of the porous layer

\[ X^* = 1, \quad -\frac{t_p}{t_f + t_p} < Y^* < 0, \quad \langle u_p \rangle^* = 0, \quad \langle v_p \rangle^* = 0 \]  
\[ (3.91) \]

(7) BC#7-bottom wall of the porous layer

\[ 0 \leq X^* \leq 1, \quad Y^* = -\frac{t_p}{t_f + t_p}, \quad \langle u_p \rangle^* = 0, \quad \langle v_p \rangle^* = 0 \]  
\[ (3.92) \]

As matter of fact, due to the thickness or deep of the flow channel is much smaller than the length of the flow channel in this studies

\[ t_f \ll L \]  
\[ (3.93) \]

\( v_f \) and \( \langle v_p \rangle \) can be neglected compared with \( u_f \) and \( \langle u_p \rangle \). The primary flow patterns in the flow channel and the porous layer are considered along the X-axis. Then, the primary dynamic motions in the flow channel and the porous layer are as follows

\[ \rho u_f \frac{\partial u_f}{\partial X} = -\frac{\partial p_f}{\partial X} + \mu \left( \frac{\partial^2 u_f}{\partial X^2} + \frac{\partial^2 u_f}{\partial Y^2} \right) \]  
\[ (3.94) \]

\[ 0 = -\varepsilon \nabla \langle p_p \rangle + \mu \varepsilon \nabla^2 \langle u_p \rangle - \mu k^{-1} \langle u_p \rangle \]  
\[ (3.95) \]

The normalized forms of flow dynamic motions in the flow channel and porous layer are simplified in mentioned equation (3.72) and equation (3.80), respectively. Clearly, it can
be seen that $u_\tau^*$ and $<u_p>^*$ are related to $t_\tau$, $t_p$, $L$, $Re$, $k$ and $\varepsilon$ in equation (3.72) and equation (3.80). The average value for velocity along $Y$-axis cross section in the flow channel and average superficial velocity along $Y$-axis in the porous layer for different value of $X$ are defined

$$u_{\text{avg}}(X) = \frac{1}{t_\tau} \int_{0}^{t_\tau} u_f(X,Y)\,dY$$  (3.96)

$$<u_p>_{\text{avg}}(X) = \frac{1}{t_p} \int_{-t_p}^{0} (u_p)(X,Y)\,dY$$  (3.97)

Equations (3.96) and equation (3.97) define the average velocity $u_{\text{avg}}$ and $<u_p>_{\text{avg}}$ at a certain $X$ location along $Y$-axis cross section. Similarly, $(u_{\text{avg}})_{fc}$ and $(<u_p>_{\text{avg}})_{pl}$ along the whole flow channel and the whole porous layer in both $X$-axis and $Y$-axis are derived as

$$(u_{\text{avg}})_{fc} = \frac{1}{t_{\tau L}} \int_{0}^{L} \int_{-t_\tau}^{t_\tau} u_f(X,Y)\,dX\,dY$$  (3.98)

$$(<u_p>_{\text{avg}})_{pl} = \frac{1}{t_{p L}} \int_{0}^{L} \int_{-t_p}^{0} (u_p)(X,Y)\,dX\,dY$$  (3.99)

Mass flow conservation along $Y$-axis from $-t_p$ to $t_\tau$ for any $X$ value gives

$$Q_{in} = Q_f(X) + Q_p(X)$$  (3.100)

Here, $Q_{in}$ is inlet mass flow per width of the flow channel, $Q_f(X)$ is the mass flow per width of the flow channel at a certain $X$ and $Q_p(X)$ is the mass flow per width of the porous layer.
at a certain \( X \). It also can be referred that \( u_{\text{avg}} \) and \( <u_p>_{\text{avg}} \) at a specific \( X \) location with assuming the same width of the flow channel and the porous layer should be satisfied

\[
(u_p)_{\text{avg}}(X) = \frac{t_r}{t_p} (u_{\text{in}} - u_{\text{favg}}(X)) \tag{3.101}
\]

The relationship between \( (u_{\text{avg}})_{fc} \) and \( (<u_p>_{\text{avg}})_{pl} \) is satisfied in a similar form

\[
((u_p)_{\text{avg}})_{pl} = \frac{t_r}{t_p} (u_{\text{in}} - (u_{\text{favg}})_{fc}) \tag{3.102}
\]

By solving equation (3.94) and equation (3.95), \( u_t \) and \( <u_p> \) are determined. Then, \( u_{\text{favg}}(X) \), \( <u_p>_{\text{avg}}(X) \), \( (u_{\text{avg}})_{fc} \) and \( (<u_p>_{\text{avg}})_{pl} \) are obtained using equation (3.96), equation (3.97), equation (3.98) and equation (3.99). Equations (3.101) and (3.102) can be applied to verify the mass flow is conserved as flow develops. Moreover, non-dimensional forms for equation (3.98), equation (3.99), equation (3.101) and equation (3.102) are expressed as

\[
(u_{\text{favg}})^*_{fc} = \frac{t_{\text{tot}}}{t_r} \int_0^1 \int_0^{t_{\text{tot}}} u_t^* (X^*, Y^*) \text{d}X^* \text{d}Y^* \tag{3.103}
\]

\[
((u_p)_{\text{avg}})^*_{pl} = \frac{t_{\text{tot}}}{t_p} \int_0^1 \int_0^{t_{\text{tot}}} (u_p)^* (X^*, Y^*) \text{d}X^* \text{d}Y^* \tag{3.104}
\]

\[
(u_p)_{\text{avg}}^*(X^*) = \frac{t_r}{t_p} (1 - u_{\text{favg}}^*(X^*)) \tag{3.105}
\]

\[
((u_p)_{\text{avg}})^*_{pl} = \frac{t_r}{t_p} (1 - (u_{\text{favg}})^*_{fc}) \tag{3.106}
\]
Where, \( t_{\text{tot}} = t_f + t_p \)

From equation (3.103) and equation (3.104), \((u_{\text{avg}})^*_f\) and \((<u_p>_{\text{avg}})^*_p\) are obtained. Also, the value of \((u_{\text{avg}})^*_f\), \((<u_p>_{\text{avg}})^*_p\), \(u_{\text{avg}}^*(X^*)\) and \(<u_p>_{\text{avg}}^*(X^*)\) can be verified through equation (3.105) and equation (3.106).
3.5 Summary

The complete dimensional and non-dimensional models derived are summarized, also the primary flow dynamic motions and some definitions are included.

Table 3 Complete dynamic motions in the flow channel and the porous layer along X-axis and Y-axis

<table>
<thead>
<tr>
<th>Domain</th>
<th>Motions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow channel</td>
<td>[ \rho u_f \frac{\partial u_f}{\partial X} + \rho v_f \frac{\partial u_f}{\partial Y} = - \frac{\partial p}{\partial X} + \mu \left( \frac{\partial^2 u_f}{\partial X^2} + \frac{\partial^2 u_f}{\partial Y^2} \right) ]</td>
<td>X-axis</td>
</tr>
<tr>
<td></td>
<td>[ \rho u_f \frac{\partial v_f}{\partial X} + \rho v_f \frac{\partial v_f}{\partial Y} = - \frac{\partial p}{\partial Y} + \mu \left( \frac{\partial^2 v_f}{\partial X^2} + \frac{\partial^2 v_f}{\partial Y^2} \right) - \rho g ]</td>
<td>Y-axis</td>
</tr>
<tr>
<td>Porous layer</td>
<td>[ 0 = -\varepsilon \frac{\partial (p_p)}{\partial X} + \mu \left( \frac{\partial^2 (u_p)}{\partial X^2} + \frac{\partial^2 (u_p)}{\partial X^2} \right) - \mu \varepsilon k^{-1} (u_p) ]</td>
<td>X-axis</td>
</tr>
<tr>
<td></td>
<td>[ 0 = -\varepsilon \frac{\partial (p_p)}{\partial Y} + \mu \left( \frac{\partial^2 (v_p)}{\partial Y^2} + \frac{\partial^2 (v_p)}{\partial Y^2} \right) - \mu \varepsilon k^{-1} (v_p) - \varepsilon g ]</td>
<td>Y-axis</td>
</tr>
</tbody>
</table>
Table 4 Primary dynamic motions in the flow channel and the porous layer along X-axis

<table>
<thead>
<tr>
<th>Domain</th>
<th>Motions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow channel</td>
<td>$\rho u_f \frac{\partial u_f}{\partial X} = -\frac{\partial p}{\partial X} + \mu \left( \frac{\partial^2 u_f}{\partial X^2} + \frac{\partial^2 u_f}{\partial Y^2} \right)$</td>
<td>(3.94)</td>
</tr>
<tr>
<td>Porous layer</td>
<td>$0 = -\varepsilon \frac{\partial (p_p)}{\partial X} + \mu \left( \frac{\partial^2 (u_p)}{\partial X^2} + \frac{\partial^2 (u_p)}{\partial Y^2} \right) - \mu \kappa^{-1} (u_p)$</td>
<td>(3.95)</td>
</tr>
</tbody>
</table>

Table 5 Non-dimensional forms for complete dynamic model along X-axis and Y-axis

<table>
<thead>
<tr>
<th>Domain</th>
<th>Motions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow channel</td>
<td>$Re \left( \frac{(t_f+t_p)^2}{t_f L} u_f^* \right) \frac{\partial u_f^<em>}{\partial X^</em>} + Re \left( \frac{(t_f+t_p)^2}{t_f} v_f^* \right) \frac{\partial v_f^<em>}{\partial Y^</em>} = -Re \left( \frac{(t_f+t_p)^2}{t_f L} \right) \frac{\partial p_f^<em>}{\partial X^</em>} + \frac{(t_f+t_p)^2}{L^2} \frac{\partial^2 u_f^<em>}{\partial X^{2</em>}} + \frac{\partial^2 v_f^<em>}{\partial Y^{2</em>}}$</td>
<td>X-axis (3.72)</td>
</tr>
<tr>
<td>Porous layer</td>
<td>$-\varepsilon Re \left( \frac{\partial (p_p)^<em>}{\partial X^</em>} \right) + \frac{1}{L^2} \frac{\partial^2 ((u_p)_p)^<em>}{\partial (X^</em>)^2} + \frac{1}{(t_f+t_p)^2} \frac{\partial^2 (u_p)_p^<em>}{\partial (Y^</em>)^2} - \frac{\varepsilon}{\kappa} (u_p)_p^* = 0$</td>
<td>X-axis (3.80)</td>
</tr>
</tbody>
</table>
\[- \frac{\varepsilon \text{Re}}{t_f(t_f + t_p)} \frac{\partial^2 (v_p^*)}{\partial (Y^*)^2} + \frac{1}{L^2} \frac{\partial^2 (v_p^*)}{\partial (X^*)^2} + \frac{1}{(t_f + t_p)^2} \frac{\partial}{\partial (Y^*)} \left( \frac{\partial (v_p^*)}{\partial (Y^*)} \right) - \frac{\varepsilon \mu}{\mu u_{in}} = 0 \]

Y-axis \hspace{1cm} (3.82)

Table 6 Non-dimensional forms for primary dynamic model along X-axis

<table>
<thead>
<tr>
<th>Domain</th>
<th>Motions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow channel</td>
<td>( \text{Re} \frac{(t_f + t_p)^2}{t_f L} u_f^* \frac{\partial u_f^<em>}{\partial X^</em>} + \text{Re} \frac{(t_f + t_p)}{t_f} v_f^* \frac{\partial v_f^<em>}{\partial Y^</em>} = -\text{Re} \frac{(t_f + t_p)^2}{t_f L} \frac{\partial p_f^<em>}{\partial X^</em>} + \frac{(t_f + t_p)^2}{L^2} \frac{\partial^2 u_f^<em>}{\partial (Y^</em>)^2} + \frac{\partial^2 u_f^<em>}{\partial (Y^</em>)^2} )</td>
<td>(3.72)</td>
</tr>
<tr>
<td>Porous layer</td>
<td>(- \varepsilon \text{Re} \frac{\partial (v_p^<em>)}{\partial (X^</em>)} + \frac{1}{L^2} \frac{\partial^2 (u_p^<em>)}{\partial (X^</em>)^2} + \frac{1}{(t_f + t_p)^2} \frac{\partial}{\partial (Y^<em>)} \left( \frac{\partial (u_p^</em>)}{\partial (Y^<em>)} \right) - \frac{\varepsilon}{k} \left( u_p^</em> \right) = 0 )</td>
<td>X-axis</td>
</tr>
</tbody>
</table>

Table 7 Dimensional boundary conditions for the primary dynamic motion along X-axis

<table>
<thead>
<tr>
<th>Type</th>
<th>Boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>( X = L, 0 \leq Y \leq t_f, u_f = u_{in} )</td>
</tr>
<tr>
<td>#2</td>
<td>( 0 &lt; X &lt; L, Y = t_f, u_f = 0 )</td>
</tr>
<tr>
<td>#3</td>
<td>( X = L, 0 \leq Y \leq t_f, p_f = 0 )</td>
</tr>
<tr>
<td>#4</td>
<td>( 0 &lt; X &lt; L, Y = 0, u_f(\Sigma_p) = (u_p)(\Sigma_p) )</td>
</tr>
</tbody>
</table>
\[
0 < X < L, \ Y = 0, \ p_r(\Sigma_{fp}) = (p_p)(\Sigma_{pf})
\]

\[
0 < X < L, \ Y = 0, \ \frac{\partial u_f}{\partial Y}(\Sigma_{fp}) = \frac{1}{\varepsilon} \frac{\partial (u_p)}{\partial Y} (\Sigma_{pf})
\]

<table>
<thead>
<tr>
<th>Type</th>
<th>Normalized boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>#5</td>
<td>( X = 0, \ -t_p &lt; Y &lt; 0, \ (u_p) = 0 )</td>
</tr>
<tr>
<td>#6</td>
<td>( X = L, \ -t_p &lt; Y &lt; 0, \ (u_p) = 0 )</td>
</tr>
<tr>
<td>#7</td>
<td>( 0 \leq X \leq L, \ Y = -t_p, \ (u_p) = 0 )</td>
</tr>
</tbody>
</table>

Table 8 Non-dimensional boundary conditions for the primary dynamic motion along X-axis

<table>
<thead>
<tr>
<th>Type</th>
<th>Normalized boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>( X^* = 0, \ 0 \leq Y^* \leq \frac{t_f}{t_f + t_p}, \ u_f = u_{in} )</td>
</tr>
<tr>
<td>#2</td>
<td>( 0 &lt; X^* &lt; 1, \ Y^* = \frac{t_f}{t_f + t_p}, \ u_f^* = 0 )</td>
</tr>
<tr>
<td>#3</td>
<td>( X^* = 1, \ 0 \leq Y^* \leq \frac{t_f}{t_f + t_p}, \ p_f^* = 0 )</td>
</tr>
<tr>
<td>#4</td>
<td>( 0 &lt; X^* &lt; 1, \ Y^* = 0, \ u_f^<em>(\Sigma_{fp}) = (u_p)^</em>(\Sigma_{pf}) )</td>
</tr>
<tr>
<td></td>
<td>( 0 &lt; X^* &lt; 1, \ p_f^<em>(\Sigma_{fp}) = (p_p)^</em>(\Sigma_{pf}) )</td>
</tr>
<tr>
<td></td>
<td>( 0 &lt; X^* &lt; 1, \ \frac{\partial u_f^<em>}{\partial Y}(\Sigma_{fp}) = \frac{1}{\varepsilon} \frac{\partial (u_p)^</em>}{\partial Y} (\Sigma_{pf}) )</td>
</tr>
</tbody>
</table>
Table 9 Some definitions for the average velocities in the flow channel and the porous layer

<table>
<thead>
<tr>
<th>Definitions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_{f_{avg}}(X) = \frac{1}{t_f} \int_0^{t_f} u_f(X,Y) , dY$</td>
<td>(3.96)</td>
</tr>
<tr>
<td>$(u_p)<em>{avg}(X) = \frac{1}{t_p} \int</em>{-t_p}^{0} (u_p)(X,Y) , dY$</td>
<td>(3.97)</td>
</tr>
<tr>
<td>$(u_{f_{avg}})<em>{fc} = \frac{1}{t_f t</em>{tot}} \int_0^L \int_0^{t_f} u_f(X,Y) , dX , dY$</td>
<td>(3.98)</td>
</tr>
<tr>
<td>$(u_{f_{avg}})<em>{pl} = \frac{1}{t_p t</em>{tot}} \int_0^L \int_{-t_p}^0 (u_p)(X,Y) , dX , dY$</td>
<td>(3.99)</td>
</tr>
<tr>
<td>$(u_{p_{avg}})<em>{avg} = \frac{t_f}{t_p} (u</em>{in} - u_{f_{avg}}(X))$</td>
<td>(3.101)</td>
</tr>
<tr>
<td>$(u_{p_{avg}})<em>{pl} = \frac{t_f}{t_p} (u</em>{in} - (u_{f_{avg}})_{fc})$</td>
<td>(3.102)</td>
</tr>
<tr>
<td>$(u_{f_{avg}}^\ast)<em>{fc} = \frac{t</em>{tot}}{t_f} \int_0^1 \frac{t_f}{t_{tot}} \int_0^{t_f} u_f^\ast(X^\ast, Y^\ast) , dX^\ast , dY^\ast$</td>
<td>(3.103)</td>
</tr>
<tr>
<td>$(u_{p_{avg}}^\ast)<em>{pl} = \frac{t</em>{tot}}{t_p} \int_0^1 \frac{t_p}{t_{tot}} \int_0^{t_p} (u_p)^\ast(X^\ast, Y^\ast) , dX^\ast , dY^\ast$</td>
<td>(3.104)</td>
</tr>
<tr>
<td>$(u_{p_{avg}}^\ast(X^\ast)) = \frac{t_f}{t_p} (1 - u_{f_{avg}}^\ast(X^\ast))$</td>
<td>(3.105)</td>
</tr>
</tbody>
</table>
\[(u_p)^*_{avg} \equiv \frac{t_f}{t_p} (1 - (u_{avg}^*)_{fc}) \]  

(3.106)
CHAPTER IV: Pre-computational Analysis

4.1 Physical parameters

Before employing computational fluid dynamics (CFD) solver based on the discretized domain, boundary conditions and related algorithms, 2D physical parameters are determined, including the flow channel length (L), thickness ($t_f$) and width ($w_f$) of the flow channel $\Omega_f$, thickness ($t_p$) of the porous electrode or porous layer $\Omega_p$, electrolyte density ($\rho$) and dynamic viscosity ($\mu$), pore or fiber diameter ($d_{po}$ or $d_{fi}$), porosity ($\varepsilon$) and permeability ($k$) of the porous layer. Related parameters for geometry, electrolyte properties and operating conditions are given in Table 12. The RFB flow cell with the serpentine flow channel is evolved from the direct methanol fuel cell (DMFC) or proton exchange membrane fuel cell (PEMFC) laboratory cell hardware, and the thickness, width and length for a single passage of the serpentine flow channel are measured to be 1mm, 1mm and 20mm, respectively. The thickness for a single layer of carbon fiber paper is ~0.41mm. The thickness of porous layer will be altered from 0.41mm to 2.87mm (the number of porous layers used ranges from 1 to 7) to investigate the effects of ratios between $t_p$ and $t_{tot}$ or ($t_p+t_f$) ranging from 0.291 to 0.742 on the mass flow transport from the flow channel to the porous layer. This model is considered as isothermal with an approximation as the working temperature of 298K [63]. The density and dynamic viscosity of electrolyte are also given in Table 12. Also, the geometry dimensions of the porous electrode and the electrolyte for most of RFBs are summarized in Table 10 and Table 11, respectively. A.A. Shah et al. [13-17], Gang Qiu et al. [64] treated the bulk electrolyte as water while K.W. Knehr et al. [12] found the density and dynamic viscosity of negative and positive electrolyte was slightly
different. The entrance volumetric flow rate $\omega_{\text{in}}=20\text{ml min}^{-1}$ gives $u_{\text{in}}=33.3\text{cm s}^{-1}$ based on the dimension of the cross section of the flow channel and $\omega_{\text{in}}$ will be altered from $5\text{ml min}^{-1}$ ($u_{\text{in}}=8.3\text{cm s}^{-1}$) to $30\text{ml min}^{-1}$ ($u_{\text{in}}=50\text{cm s}^{-1}$) to study the entrance volumetric flow rates on the mass flow penetration into the porous layer. Table 13 gives properties of the porous layer, including three kinds of foametal, carbon fiber paper or carbon felt and graphite felt porous material. The foametal specimens were used in the experimental studies of Beavers and Joseph [40] to analyze the boundary conditions of the Poiseuille flow over a permeable interface. Carbon fiber paper or carbon felt [28] and graphite felt [24] are typical porous materials for the porous electrodes in the RFB flow cells.

Table 10 2D physical dimensions for the porous electrodes in most RFBs

<table>
<thead>
<tr>
<th>$t_p$(mm)×$L$(mm)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>4×100</td>
<td>[13,14,16,17]</td>
</tr>
<tr>
<td>3×77</td>
<td>[18]</td>
</tr>
<tr>
<td>3×100</td>
<td>[24]</td>
</tr>
<tr>
<td>0.41×(NG*)</td>
<td>[21]</td>
</tr>
<tr>
<td>0.3×12</td>
<td>[33]</td>
</tr>
</tbody>
</table>

NG*: Not Given
Table 11 Properties of flowing electrolyte in vanadium RFBs

<table>
<thead>
<tr>
<th>ρ [kg/m³]</th>
<th>µ [Pa*s]</th>
<th>Flow cells</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>8×10⁻³</td>
<td>Vanadium</td>
<td>[33]</td>
</tr>
<tr>
<td>1000</td>
<td>1×10⁻³</td>
<td></td>
<td>[13,14,16,17,64]</td>
</tr>
<tr>
<td>-1300</td>
<td>-2.5×10⁻³</td>
<td></td>
<td>[12]</td>
</tr>
<tr>
<td>+1350</td>
<td>+5×10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>1.605×10⁻³</td>
<td>Vanadium</td>
<td>[24]</td>
</tr>
<tr>
<td>1354</td>
<td>4.928×10⁻³</td>
<td></td>
<td>[63]</td>
</tr>
</tbody>
</table>

Table 12 Geometry, electrolyte properties and operation parameters in this studies

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of flow channel (t₁)</td>
<td>1mm</td>
<td>Measured</td>
</tr>
<tr>
<td>Width of flow channel (w₁)</td>
<td>1mm</td>
<td>Measured</td>
</tr>
<tr>
<td>Length of flow channel (L)</td>
<td>20mm</td>
<td>Measured</td>
</tr>
<tr>
<td>Thickness of a single porous layer(tₚ)</td>
<td>0.41mm</td>
<td>[21]</td>
</tr>
<tr>
<td>Density of electrolyte (ρ)</td>
<td>1.354 g cm⁻³</td>
<td></td>
</tr>
<tr>
<td>Dynamic viscosity of electrolyte (µ)</td>
<td>4.928×10⁻³ Pa*s</td>
<td>[63]</td>
</tr>
<tr>
<td>Working temperature (T)</td>
<td>298.15 K</td>
<td></td>
</tr>
<tr>
<td>Initial ion concentration (c)</td>
<td>1mol L⁻¹</td>
<td>[21]</td>
</tr>
<tr>
<td>Entrance volumetric flow rate (ωₘ)</td>
<td>20ml min⁻¹ &amp; 20ml min⁻¹ to 30ml min⁻¹</td>
<td>[12,21]</td>
</tr>
</tbody>
</table>
Table 13 Properties of porous samples

<table>
<thead>
<tr>
<th>Porous sample</th>
<th>Pore (d_p) or fiber (d_f) diameter, [µm]</th>
<th>Porosity ε</th>
<th>Permeability k, [m²]</th>
<th>Estimated permeability (k_{ec}), [m²]*</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foametal A</td>
<td>406 (pore)</td>
<td>0.78</td>
<td>9.7×10^-9</td>
<td>8.979×10^-9</td>
<td>[46,49]</td>
</tr>
<tr>
<td>Foametal B</td>
<td>864 (pore)</td>
<td>0.78</td>
<td>3.94×10^-8</td>
<td>4.066×10^-8</td>
<td></td>
</tr>
<tr>
<td>Foametal C</td>
<td>1140 (pore)</td>
<td>0.79</td>
<td>8.2×10^-8</td>
<td>8.072×10^-8</td>
<td></td>
</tr>
<tr>
<td>Carbon fiber paper or carbon felt</td>
<td>10 (fiber)</td>
<td>0.8</td>
<td>2.0×10^-11</td>
<td>2.306×10^-10</td>
<td>[28]</td>
</tr>
<tr>
<td>Graphite felt</td>
<td>17.6 (fiber)</td>
<td>0.7</td>
<td>Not given</td>
<td>2.127×10^-10</td>
<td>[24]</td>
</tr>
</tbody>
</table>

* Estimated by equation (4.1)

Pore diameters are given for foametal A, foametal B and foameter C while fiber diameter are given for the carbon fiber paper, carbon felt and graphite felt. B. Goyeau et al. [46] made estimations of the porosity for foametal mentioned in Table 13, and the Kozeny-Carman model [65,66] shown as equation (4.1) is used to predict the permeability of porous samples

\[
k = \frac{d^2 \varepsilon^3}{c_{kc}(1-\varepsilon)^2} \quad (4.1)
\]

Where, d is the pore diameter or fiber diameter. The permeability is directly correlated with pore diameter or fiber diameter while inversely correlated with the Kozeny-Carman constant. There is a non-linear relationship between the permeability and porosity under a fixed pore diameter or fiber diameter. Carman pointed out that experimental \(C_{kc}\) was around 180 for the pore diameter. Shah et al. [13-17] and Qiu et al. [64] considered \(C_{kc}\) as 5.55
for the fiber diameter, then the estimated permeability of the carbon fiber paper or carbon felt \((d_f=10\,\mu m, \varepsilon=0.8)\) is around \(2.306 \times 10^{-10} m^2\) and this is consistent with Tomadakis et al. \cite{67} who thought the permeability was \(1 \times 10^{-10} m^2\) as a 3D random fiber model was built for the carbon fiber paper or carbon felt with 10µm fiber diameter and 0.8 porosity. However, Adam et al. \cite{28} considered the permeability as \(2 \times 10^{-11} m^2\) for the carbon fiber paper and carbon felt in Table 13. In this study, the value of \(2.306 \times 10^{-10} m^2\) is employed for the estimated permeability of the typical carbon fiber paper or carbon felt with 10µm fiber diameter and 0.8 porosity. The permeability of the graphite felt is predicted from equation (4.1) as \(2.127 \times 10^{-10} m^2\). The relationship between permeability and pore or fiber diameter under a specific porosity is shown in Fig. 4-1, the permeability is predicted through Kozeny-Carman model with considering \(C_{kc}=180\) for the pore diameter and \(C_{kc}=5.55\) for the fiber diameter.
Figure 4-1 Schematic diagram of the relationship between pore or fiber diameter and permeability under specific porosities mentioned in Table 1 is curved through using Kozeny-Carman model: (a) foametal: ●-ε=0.78, k=9.7×10^{-9}m^2; ■-ε=0.78, k=3.94×10^{-8}m^2; ◄-ε=0.79, k=8.2×10^{-8}m^2 and (b) carbon fiber paper or carbon felt: ▲-ε=0.8, k=2.306×10^{-10}m^2; graphite felt: ▼-ε=0.7, k=2.127×10^{-10}m^2
Pore and fiber diameter have a great effect on the permeability. Increasing the pore diameter from 100µm to 1000µm or fiber diameter from 10µm to 20µm, the permeability is elevated by a factor of 100 and 4 for the pore diameter and fiber diameter, respectively. Active surface area ($a_s$) of porous fibers can be estimated by the Filament Analogue model developed by Carta et al. [68] within establishing the porous fibers as cylinder models shown in equation (4.2)

$$a_s = \frac{4(1-\varepsilon)}{d_{fi}} \tag{4.2}$$

The variation of the active surface area with fiber diameter is shown in Fig. 4-2 for the carbon fiber paper (or carbon felt) and the graphite felt. The fiber diameter strongly affects the active surface area. Increasing the fiber diameter from 5µm to 15µm, the active surface area is decreased by a factor of 3. As fiber diameter ranges from 1 to 20µm, the active surface area increases from 40,000 to 800,000 m² m⁻³ or (400 cm² cm⁻³ to 8,000 cm² cm⁻³) for the carbon fiber paper or carbon felt with $\varepsilon$=0.8 and increases from 60,000 to 1,200,000 m² m⁻³ or (600 cm² cm⁻³ to 12,000 cm² cm⁻³) for the graphite felt with $\varepsilon$=0.7. However, porous fibers in reality are not perfect cylinders, and the complex shapes of the porous solids are beyond our discussions. The tradeoff between the permeability and the active surface area needs further study.
Figure 4-2 The variations of active surface area ($a_s$) for the carbon fiber paper or carbon felt and the graphite felt as the fiber diameter increases from 1µm to 20µm by using the Filament Analogue Model [59] within building porous fibers as cylinder models.
The values for the entrance volumetric flow rates, inlet velocities and Reynolds numbers are given in Table 14. Because the Reynolds number ranged from 22.8 to 137.4, the flow regime is strictly laminar flow.

Table 14 Value for $\omega_{in}$, $u_{in}$ and Re using geometry given in Table 12

<table>
<thead>
<tr>
<th>Entrance volumetric flow rates $\omega_{in}$ (ml min$^{-1}$)</th>
<th>Inlet velocities $u_{in}$ (cm s$^{-1}$)</th>
<th>Reynolds number (Re)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.3</td>
<td>22.8</td>
</tr>
<tr>
<td>10</td>
<td>16.7</td>
<td>45.9</td>
</tr>
<tr>
<td>15</td>
<td>25</td>
<td>68.7</td>
</tr>
<tr>
<td>20</td>
<td>33.3</td>
<td>91.5</td>
</tr>
<tr>
<td>25</td>
<td>41.7</td>
<td>114.6</td>
</tr>
<tr>
<td>30</td>
<td>50</td>
<td>137.4</td>
</tr>
</tbody>
</table>
CHAPTER V: Results and Discussion

5.1 Unstructured meshing & refinement

The multi-physical package CFD solver COMSOL software based on the finite element method has been used in this computational studies. The type of mesh employed is advancing front triangular unstructured grid. Compared with a conventional triangular grid, the advancing front triangular grid has a higher mesh quality and it costs less time to come to a convergence. The importance of the mesh density around the interface between the flow channel and the porous layer leads to a refinement of the grids neighbor-hooding the interface.
5.2 Grids independent analysis

The grid-independence of the results is also investigated to ensure the results are not dependent on the mesh density. For example, six different grids are made for each case (from single porous layer to seven porous layers) using carbon fiber paper or carbon felt: k=2.306×10^{-10}m^2, ε=0.8 and the average velocity (u_{avg})_{fc} in the flow channel and the average velocity (<u_{p}>_{avg})_{pl} in the porous layer with the number of grids are shown in Fig. 5-1 (the case of single porous layer is not shown). Similar grids independence analyses are also made for Foametal A (k=9.7×10^{-9}m^2, ε=0.8), Foametal B (k=3.94×10^{-8}m^2, ε=0.78), Foametal C (k=8.2×10^{-8}m^2, ε=0.79) and graphite felt (k=2.127×10^{-10}m^2, ε=0.7) for different inlet volumetric flow rates from 5ml min^{-1} to 30ml min^{-1} (u_{in} from 8.3cm s^{-1} to 50cm s^{-1}) and different thickness of the porous layer to study the mass flow transport from the flow channel into the porous layer.
Figure 5-1 The tendency between \( <u_{p_{av}} > \) and grids number (GN) as the number of porous layer increases from 2 to 7 for the carbon fiber paper or carbon felt mentioned in Table 13 \((u_{m}=33.3\text{cm s}^{-1})\)

From Fig. 5-1, it can be seen that as the number of grids reaches a certain value, the quantity \( <u_{p_{av}} > \) gradually comes to a constant. Taking two and seven porous layers we find: (1) for two porous layers, when GN reaches to 16767, \( <u_{p_{av}} > \) increases from 0.145 cm s\(^{-1}\) to 0.146 cm s\(^{-1}\), then \( <u_{p_{av}} > \) is not changed as GN increases to 131608; (2) for seven porous layers, as GN approaches to 45713, \( <u_{p_{av}} > \) climbs from 0.093 cm s\(^{-1}\) to 0.094 cm s\(^{-1}\). \( <u_{p_{av}} > \) is stable as GN increases to 416840. For the single porous layer, \( <u_{p_{av}} > \)
becomes to 0.204 cm s\textsuperscript{-1} as a stable value after GN is refined to 11405. The grid refinements ensure the fidelity of the computational results from a mesh perspective. All the results discussed below are grids independent.
5.3 Comparisons between “no slip” & “slip” for BC#7

The X-axis velocity distributions along Y-axis cross section for the fully developed region is compared between “no slip” and “slip” boundary conditions for BC#7 as shown in Fig. 5-2. Under both “no slip” and “slip” boundary conditions, the flow velocity distribution curves are similar. Compared with “no slip” BC#7, more mass flow goes into the porous layer and it brings less mass flow in the flow channel for “slip” BC#7.

Figure 5-2 X-axis velocity distributions along Y-axis: “no slip” and “slip” for BC#7 (k=9.7×10⁻⁹ m², ε=0.78, \(u_0=33.3\) cm s⁻¹, fully developed region, single porous layer)
Figure 5.3 X-axis velocity distributions along Y-axis: “no slip” and “slip” for BC#7 ($k=2.306 \times 10^{-10} \text{m}^2$, $\varepsilon=0.8$, $u_{in}=33.3 \text{cm s}^{-1}$, fully developed region, single porous layer)
The X-axis velocity distribution curves along Y-axis in fully developed region are also shown in Fig. 5-3 for carbon fiber paper or carbon felt. There is less difference between the effects from “no slip” and “slip” BC#7 on the flow distributions compared with the Foametal A (k=9.7×10⁻⁹m², ε=0.78) porous material. Fig. 5-3 (a), (b) and (c) are the enlarged local curves for the superficial velocity in the porous layer. As mentioned in chapter 3, BC#7 is preferred set as “no slip” boundary condition and this is based on the stationary ion selective membrane.
5.4 Normalized flow patterns

The flow hydrodynamics are dominated by Navier-Stokes motions in the flow channel $\Omega_f$ and Brinkman-Darcy model in the porous layer $\Omega_p$. Fig. 5-4 describes the trend of normalized $u_f^*$ and $\langle u_p \rangle^*$ along $X^*$ ranging from 0 to 1 for six different locations under the ideal plug flow inlet condition: $Y^* = 0.284$ ($Y = 0.4\text{mm}$), $Y^* = 0.319$ ($Y = 0.45\text{mm}$) and $Y^* = 0.390$ ($Y = 0.55\text{mm}$) for $\Omega_f$ and $Y^* = -0.213$ ($Y = -0.3\text{mm}$), $Y^* = -0.142$ ($Y = -0.2\text{mm}$) and $Y^* = -0.074$ ($Y = -0.1\text{mm}$) for $\Omega_p$ as Re (Reynolds number) is 91.5, which is much smaller than 2300 as the critical Reynolds number for laminar flow regime. In the $\Omega_f$ domain, $u_f^*$ climbs from 1 to 1.4 as the flow regime changes from developing to fully developed state. However, at near the edge of the $\Omega_p$ region, $\langle u_p \rangle^*$ sharply increases to a peak value, then decreases as the fully developed region is approached. The hydrodynamic entrance length $L_e^*$ is calculated to be 4.60mm as the centerline velocity is 99% of the fully developed centerline velocity. The latter is defined as the line for the maximum velocity in the X-axis. The value of the Y-axis location for the maximum velocity is .0.45mm. This is slightly smaller than the physical centerline 0.5mm along Y-axis. About 75% of the flow channel is fully developed. For the case of conventional pipes or circular ducts, the normalized entrance length $L_e^*$ is .6% of Reynolds number for laminar flow. Atkinson et al. [69] and Chen et al. [70] proposed correlations (equation (5.1) and equation (5.2)) between the non-dimensional hydrodynamic flow entrance length $L_e^*$ and the Reynolds number for a laminar flow-through the parallel plate flow channel.
\[ L_e^* = C_1 + C_2 \text{Re} \]  
(5.1)

\[ L_e^* = \frac{C_3}{(C_4 \text{Re} + 1)} + C_5 \text{Re} \]  
(5.2)

Here, \( L_e^* = L_e / t_f \), \( C_1 = 0.625 \), \( C_2 = C_5 = 0.044 \), \( C_3 = 0.63 \), \( C_4 = 0.035 \)

Figure 5.4 The trend of normalized \( u_f^* \) and \( <u_p>^* \) with \( X^* \) from 0 to 1 at six \( Y^* \): 0.390, 0.319, 0.284, -0.071, -0.142 and -0.213 in \( \Omega_f \) and \( \Omega_p \) (\( k = 9.7 \times 10^{-9} \text{m}^2 \), \( \varepsilon = 0.78 \), \( \text{Re} = 91.5 \), \( t_f = 1 \text{mm} \), \( t_p = 0.41 \text{mm} \)), ideal plug flow inlet

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Figure 5-5 The enlarged local curves of Figure 5-4 (a)

Using correlations (5.1) and (5.2), the corresponding estimated $L_e$ are 4.65mm and 4.18mm. These entrance length predictions have reasonable agreement with the numerically computed entrance length of 4.6mm. Some back flow occur in the porous layer with a small value of $X^*$ as shown in Fig. 5-5. Using a lower entrance volumetric flow rate ($\omega=5\text{ml min}^{-1}$) of $u_{in}=8.3\text{cm s}^{-1}$ and $Re=22.8$, $L_e$ is computed to be 1.34mm. Thus, the extent of the fully developed region is over 98% of the flow channel length (see Fig. 5-6). The estimated $L_e$ from equation (5.1) and equation (5.2) are seen to be in reasonable agreement with computed results of 1.34mm at 1.63mm and 1.35mm, respectively.
Moreover, if $\omega_{in}$ is in the range of 20 ml min$^{-1}$ to 30 (Knehr et al. [111]), and then $u_{in}$ ranges from 33.3 cm s$^{-1}$ to 50 cm s$^{-1}$ (Re ranges from 91.5 to 137.4). The corresponding values of $L_e$ then lie in the range of 4.6 mm to 6.7 mm. This illustrates that roughly 65% to
75% part of the flow channel is fully developed. Thus, it is seen that it is not correct to estimate the average flow velocity of the whole flow channel and the whole porous layer just using the average velocity in fully developed region. In later discussions, volume flow rates of $\omega_{in}=20\text{ml min}^{-1}$ ($u_{in}=33.3\text{cm s}^{-1}$) are used to analyze the maximum current density for the carbon fiber paper and compared with the experimental results from Aaron et al.\textsuperscript{[20]}. It is emphasized that for our model is not exactly the same at that for a parallel flow plate channel. For the latter, the BC#4 should be “no slip” instead of continuity of filtration velocity and normal stress mentioned in Table 1. Thus, some accuracy is lost for the entrance length prediction when correlations (5.1) and (5.2) are
used. Compared with back flow as shown in Fig. 5-5, the back flow is less intense as shown in Fig. 5-7. It can be referred that the back flow is more evident with a larger Reynolds number under the ideal plug flow inlet condition. From both Fig. 5-4 and Fig. 5-6, a shoot (means a dramatic increase) is found in the velocity profile of the porous layer with a small $X^*$, the possible reason is that the interface forwarding flow momentum push the fluid with a fast penetration near to the left wall (BC#5) of the porous layer under the ideal plug flow inlet condition. However, the shoot disappears when the ideal parabolic flow inlet condition is adopted and the normalized velocity $<u_p>*$ profile along $X*$ for different $Y*$ in the porous layer is shown in Fig. 5-8. The only difference between the model for Fig. 5-4 and Fig. 5-8 is the inlet boundary condition. Clearly, almost no shoot occurs in Fig. 5-8 under the ideal parabolic flow inlet condition. A possible explanation is that the entrance interface velocity is zero, and no large flow momentum could drag the flow with a large penetration into the porous layer under the ideal parabolic flow inlet condition. Fig. 5-9 reveals that back flow also occurs under the ideal parabolic flow inlet condition. The phenomena of the shoot and back flow also could be explained through the pressure distributions along $X*$. For example, Fig. 5-10 shows the normalized pressure distribution along $X*$ in the flow channel and the porous layer as Reynolds number is 91.5 under the ideal plug flow inlet. Fig. 5-11 and Fig. 5-12 are the enlarged local curves of Fig. 5-10 (a) and (b), respectively. As $X*$ ranges from -0.15 to -0.9, the non-dimensional $p_f*$ is equal to $<p_p>*$. However, $p_f*$ is larger than $<p_p>*$ when $X*$ is from 0 to -0.03, then the mass flow penetration increases a lot in the porous layer. When $X*$ is from -0.03 to -0.15, $p_f*$ is slightly smaller than $<p_p>*$, which hinders flow penetration into the porous layer and the
The trend of normalized $u_f^*$ and $<u_p>^*$ with $X^*$ from 0 to 1 at six $Y^*$: 0.390, 0.319, 0.284, -0.071, -0.142 and -0.213 in $\Omega_f$ and $\Omega_p$ (k=9.7×10⁻⁹m², $\varepsilon=0.78$, Re=91.5, $t_f=1$mm, $t_p=0.41$mm), ideal parabolic flow inlet velocity has a decrease in the porous layer. When $X^*$ is larger than ~0.9, $<p_p>^*$ is larger than $p_r^*$, then the flow penetration into the porous layer decreases as shown in Fig. 5-4.
Figure 5.9 The enlarged part (a) of Figure 5.8

Figure 5.10 $p_i^*$ & $<p_p>^*$ with $X^*$, Re=91.5, ideal plug flow inlet
Figure 5-11 Enlarged local curves of Figure 5-10 (a)

Figure 5-12 Enlarged local curves of Figure 5-10 (b)
Fig. 5-13 describes the trend of normalized $u_\ast$ and $<u_p>_\ast$ along the normalized longitudinal cross section $Y_\ast$ from -0.291 to 0.709 for four specific values of $X_\ast$: 0, 0.1, 0.2 and 0.7 representing the entrance through the developing, developed and fully developed regions. It is seen that he normalized average velocity $u_{avg_\ast}$ decreases from 1 to 0.921, then increases to 0.934 while $<u_p>_{avg_\ast}$ exhibits an opposite tendency and climbs from 0 to 0.179, then decreases to 0.150 as the fully developed region is approached. The normalized averages $u_{avg_\ast}$ and $<u_p>_{avg_\ast}$ for $Y_\ast$ with $X_\ast$ are described by equations (5.3) and (5.4), respectively

\[
(u_{avg_\ast})_{X_\ast} = \frac{t_{tot}}{t_f} \int_0^{t_f} u_{\ast} (X_\ast, Y_\ast) dY_\ast
\]  
(5.3)

\[
(<u_p>_{avg_\ast})_{X_\ast} = \frac{t_{tot}}{t_p} \int_0^{t_p} <u_p>_\ast (X_\ast, Y_\ast) dY_\ast
\]  
(5.4)
Figure 5-13 Non-dimensionlization flow configurations for $u_f^*$ and $<u_p>*$ with $Y^*$ from inlet to developing, developed and fully developed region in $\Omega_f$ and $\Omega_p$ at four $X^*$: 0, 0.1, 0.2 and 0.7 ($k=9.7\times10^{-9}\text{m}^2$, $\varepsilon=0.78$, $Re=91.5$, $t_f=1\text{mm}$, $t_p=0.41\text{mm}$), ideal plug flow inlet

Figure 5-14 Non-dimensionlization flow configurations for $u_f^*$ and $<u_p>*$ with $Y^*$ from inlet to developing, developed and fully developed region in $\Omega_f$ and $\Omega_p$ at four $X^*$: 0, 0.1, 0.2 and 0.7 ($k=9.7\times10^{-9}\text{m}^2$, $\varepsilon=0.78$, $Re=91.5$, $t_f=1\text{mm}$, $t_p=0.41\text{mm}$), ideal parabolic flow inlet
Similarly, the Fig. 5-14 illustrates the tendency of $u_f^*$ and $<u_p>^*$ along the normalized longitudinal cross section $Y^*$ from -0.291 to 0.709 for four specific $X^*$: 0, 0.1, 0.2 and 0.7 from the parabolic entrance to developing, developed and fully developed region under the ideal parabolic flow inlet condition. The normalized average velocity $u_{\text{avg}}^*$ decreases from 1 to 0.945, then increases to 0.938 while $<u_p>_{\text{avg}}^*$ performances an opposite tendency that increases from 0 to 0.15 as the fully developed region is approached. When the fully developed region arrives, the value of $u_{\text{avg}}^*$ and $<u_p>_{\text{avg}}^*$ are almost the same under both the ideal plug flow inlet and ideal parabolic flow inlet conditions.

To illustrate the non-dimensional average velocity in the whole flow channel and the porous layer, equations (3.103) and (3.104) have been already derived. These equations describe the normalized velocity along both transverse ($X^*$) and longitudinal ($Y^*$) directions while equations (5.3) and (5.4) just give the average velocity in a specific $X^*$ along $Y^*$. If the whole flow channel is in fully developed state at small $Re$, then the difference between the integrated average velocities calculated by equation (5.3) and equation (3.103) and the integrated average velocities calculated by equation (5.4) and equation (3.104) are very small. However, this is not true at large $Re$, where the hydrodynamic entrance length is long compared with the whole flow channel.
5.5 Inlet volumetric flow rate & permeability effects

The effects from entrance volumetric flow rates on the flow distributions for the fully developed region are shown in Fig. 5-15. Clearly, the mass transfer is strengthened both in the flow channel and the porous layer as the entrance flow rate climbs from 10ml min\(^{-1}\) to 30ml min\(^{-1}\), which gives inlet velocity ranging from 16.7cm s\(^{-1}\) to 50cm s\(^{-1}\). Fig. 5-16 illustrates the effects of the permeability on the enhancement of mass flow penetration into the porous layer. It seems that the permeability has a more dominant influence than the entrance volumetric flow rates on the increase of mass flow in the porous layer. Compared with foametal porous samples, \(\langle u_p \rangle\) is much smaller in the typical carbon fiber paper or carbon felt and graphite felt used in the RFB cells. The permeability of latter that results in much less mass flow transferred from the flow channel into the porous layer. Certainly, this diagram cannot clearly illustrate the weights between permeability and porosity.
Figure 5-15 $u_i$ and $<u_p>$ profiles along Y-axis for fully developed region: entrance volumetric flow rate climbs from 10 ml min$^{-1}$ to 30 ml min$^{-1}$ ($u_{in}$ ranges from 16.7 cm s$^{-1}$ to 50 cm s$^{-1}$, $k=9.7\times10^{-9}$ m$^2$, $\varepsilon=0.78$, $t_f=1$ mm, $t_p=0.41$ mm), ideal plug flow inlet
Figure 5-16 $u_f$ and $<u_p>$ profiles along Y-axis for fully developed region: permeability increases from $2.306 \times 10^{-10} \text{m}^2$ to $8.2 \times 10^{-8} \text{m}^2$ for the foametal and the carbon fiber paper or carbon felt porous material ($t_f=1 \text{mm}, t_p=0.41 \text{mm}, u_m=33.3 \text{cm s}^{-1}$), ideal plug flow inlet
5.6 Thickness of porous layer & flow channel effects

The effects of the thickness of the porous layer and the flow channel on the flow distributions along Y-axis have been investigated. Fig. 5-17 depicts the flow distributions for fully developed region at three different thicknesses of the porous layers: 0.41mm (single porous layer), 1.23mm (two porous layers) and 2.05mm (five porous layers) with a fixed 1mm flow channel depth.

![Graph showing flow distributions for three different thicknesses of porous layers](image)

Figure 5-17 $u_i$ & $<u_p>$ profiles along Y-axis for three different thickness of the porous layers: 0.41mm (single porous layer), 1.23mm (two porous layers) and 2.05mm (five porous layers) for fully developed region ($t_f=1\text{mm}$, $u_{in}=33.3\text{cm/s}$, $k=9.7\times10^{-9}\text{m}^2$, $\varepsilon=0.78$), ideal plug flow inlet.
Figure 5-18 $u_f$ & $<u_p>$ profiles along Y-axis for three different thickness of the flow channels: 0.4mm, 0.7mm and 1.0mm for the fully developed region ($t_f=0.41$mm, $u_{in}=33.3$cm s$^{-1}$, $k=9.7\times10^{-9}$m$^2$, $\varepsilon=0.78$), ideal plug flow inlet.

More mass flow flux is transferred from the flow channel into the porous layer with a larger $t_p$ while the filtration velocity in the porous layer exhibits an opposite trend. The influence of the depth of the flow channel is also illustrated in Fig. 5-18, more mass flow goes into the porous layer within decreasing of depth of the flow channel and the average bulk velocity in the porous layer shows a similar trend. It should be noted that
when $t_f=0.4\text{mm}$, the flow velocity does not develop to a larger value from inlet to the fully developed region in the flow channel as described in Fig. 5-19. The trend for $u_f$ and $<u_p>$ along the X-axis coordinate is different from the results shown in Fig. 5-4 and Fig. 5.6. With a 0.4mm depth of the flow channel and 0.41mm thickness of the porous layer, $u_f$
has a slight increase then decreases to a constant value while $<u_p>$ has the opposite tendency as the fully developed region is approached. The possible reason is that the small thickness of the flow channel with BC#2 and BC#4 cannot constrain the flow to obtain a large velocity as compared with a conventional parallel flow channel with both “no slip” for BC#2 and BC#4. Thus, more flow is forced into the porous layer. In order to enhance the mass flow penetrated into the porous layer, reducing the thickness of the flow channel maybe a good choice.
5.7 Mass flow

The mass flow in the flow channel and the porous layer is investigated to assess the effects of the following parameters: entrance volumetric flow rates, permeability of the porous material and thickness of the porous layer. The average flow rates throughout the porous layer ($\langle u_p^{avg} \rangle_{pl}$) with respect to $u_{in}$ and $t_p$ are shown in Fig. 5-20 and Fig. 5-21, respectively. The relationship between ($\langle u_p^{avg} \rangle_{pl}$ and inlet velocities for foameal, carbon fiber paper or carbon felt and graphite felt porous materials are illustrated in Fig. 5-20, an approximately linear relation occurs for ($\langle u_p^{avg} \rangle_{pl}$ with $u_{in}$. Compared with the foameal, ($\langle u_p^{avg} \rangle_{pl}$ is much smaller in the carbon fiber paper or carbon felt and the graphite felt used in the RFB flow cells. As $u_{in}$ climbs from 8.3cm $s^{-1}$ to 50cm $s^{-1}$ ($\omega_{in}$ from 5ml min$^{-1}$ to 30ml min$^{-1}$), ($\langle u_p^{avg} \rangle_{pl}$ increases from 0.048cm $s^{-1}$ to 0.318cm $s^{-1}$ for a single layer of the carbon fiber paper. The effects from $t_p$ on ($\langle u_p^{avg} \rangle_{pl}$ are also illustrated in Fig. 5-21. As $t_p$ climbs from 0.41mm to 2.87mm (the number of porous layer added from 1 to 7) with a fixed $t_f=1$mm, ($\langle u_p^{avg} \rangle_{pl}$ performs a decreasing behavior. Moreover, the variations of $Q_p$ ($t_p*(\langle u_p^{avg} \rangle_{pl}$) with $t_p$ are shown in Fig. 5-22, which illustrates that $Q_p$ increases gradually as the porous layer becomes thicker.
Figure 5-20 The trend of \( \langle u_p^2 \rangle_{\text{avg}, pl} \) with \( u_{\text{in}} \): (a) foametal; (b) carbon fiber paper or carbon felt and graphite felt \((t_f=1\, \text{mm}, t_p=0.41\, \text{mm})\), ideal plug flow inlet.
Figure 5-21 The trend of $(u_{p,\text{avg}})_p$ with $t_p$: (a) foametal; (b) carbon fiber paper or carbon felt and graphite felt ($u_0=33.3\text{ cm s}^{-1}$, $t_0=1\text{ mm}$), $t_p$ increases from 0.41mm to 2.87mm, ideal plug flow inlet.
Figure 5-22 The variations of $Q_p$ with $t_p$: (a) the foametal; (b) the carbon fiber paper or carbon felt and the graphite felt ($u_\infty=33.3\text{ cm s}^{-1}$, $t_f=1\text{ mm}$), $t_p$ increases from 0.41mm to 2.87mm, ideal plug flow inlet

The relationship between $(<u_p>_{\text{avg}})_{pl}$ and $t_p/t_{tot}$ for Reynolds number ranging from 22.8 to 137.4 for the typical carbon fiber paper used in the RFB flow cells is shown in Fig. 5-23. The value for $(<u_p>_{\text{avg}})_{pl}$ is relatively low. For example, as $t_p/t_{tot}$ ranges from 0.291 to 0.742 (the number of porous layers ranges from 1 to 7), $(<u_p>_{\text{avg}})_{pl}$ varies from $2.65\times10^{-3}$
to $5.78\times10^{-3}$ when $Re$ is 22.8. However, as $Re$ climbs, $(<u_p^{avg^*}>)_pl$ also shows a slight increase. As $Re$ ranges from 22.8 to 137.4, $(<u_p^{avg^*}>)_pl$ increases from $3.61\times10^{-3}$ to $3.90\times10^{-3}$ when $t_p/t_{tot}$ is 0.552 (three porous layers) while the range is $5.78\times10^{-3}$ to $6.36\times10^{-3}$ as $t_p/t_{tot}$ is 0.291 (single porous layer).

Figure 5.23 The relationship between $(<u_p^{avg^*}>)_pl$ with $t_p/t_{tot}$ as $Re$ ranging from 22.8 to 137.4 for the typical carbon fiber paper or carbon felt used in RFB flow cells ($k=2.306\times10^{-10} m^2$), ideal plug flow inlet.
5.8 Limiting and maximum current density

As electrolyte flows through the porous electrode, the chemical reactions at the electrolyte interface with the porous solid results in electrical current flow. The latter is determined by the total species flux, Faraday constant and the number of electrons transferred during the charging or discharging process. The species flux is related to diffusion, convection and electro-migration processes. The current density is constrained by a concentration over-potential that arises due to mass transfer limitations. In order to minimize the concentration over-potential, the operating current density is usually chosen to be not larger than 25% of the limiting current density (based on membrane area), which could be obtained from the Fick’s law

\[ i_{\text{lim}} = \frac{a t_p n F D c}{\delta} \]  

(5.5)

Here, \( n \) is the number of transferring electrons involved in the reactions, \( F \) is Faraday constant, \( D \) is diffusivity, \( c \) is the bulk electrolyte concentration, \( t_p \) is the thickness of the porous electrode, \( a \) is the interfacial area of reaction per unit of porous electrode volume, and \( \delta \) is the thickness of diffusion layer. Equation (5.5) also can be written as

\[ i_{\text{lim}} = a t_p n F k_m c \]  

(5.6)
Figure 5-24 (a) a thick porous electrode for the conventional RFBs; (b) a RFB flow cell with the serpentine flow channel modified from DMFC or PEMFC; (c) a single passage of the flow channel with a thin porous layer, cross section view of (b); (d) adjoin flow channels with a thin porous layer, cross section view of (b)

Where, \( k_m \) represents the local mass transfer coefficient at the surface between the porous solid and the bulk flowing electrolyte solution. A typical thickness of the conventional porous electrode in an RFB flow cell is \(~3\text{mm}\) and the typical operating current density is \(~50\text{mA cm}^{-2}\), which is limited by the large ohmic drop due to a thick porous electrode used. Recently, Aaron et al. \cite{21} designed a flow battery with serpentine flow channels modified from DMFC or PEMFC flow cell as shown in Fig. 5-24 (b), (c) and (d). Compared with the classic RFBs as shown in Fig. 5-24 (a), this flow cell has a thin porous layer (typical \(~0.4\text{mm}\)) and it can lead to a lower ohmic loss within enabling a higher limiting current density. This can be estimated by equation (5.7) \cite{71}
Where, $s$ is a stoichiometric coefficient in the porous electrode reaction. Using equation (5.7) and the following values for volumetric flow rate ($\omega_{in}=20\text{ml min}^{-1}$), the geometry for the single flow channel ($t_{f}=w_{f}=1\text{mm}$, $L=20\text{mm}$), bulk concentration ($c=1\text{M}$), diffusivity ($D=10^{-6}\text{cm}^2\text{ s}^{-1}$) and stoichiometric coefficient ($s=1$) and assuming no electrolyte penetration, the limiting current density is estimated to be 78mA cm$^{-2}$. However, this predicted value significantly underestimates the reported maximum current density ~400mA cm$^{-2}$ and ~750mA cm$^{-2}$ observed for a single layer and three layers of carbon fiber paper in reference [21], respectively. One can estimate the maximum current density limited by the total reactant consumption in the porous layer by mass balance and the Faraday’s law of electrolysis

\[
\frac{i_{\text{max}}}{u_{\text{in}}} = nF c \left( \langle u_{p} \rangle_{\text{avg}}^{*} \right)_{pl} \frac{t_{p}}{L}
\] (5.8)

Here, $\left( \langle u_{p} \rangle_{\text{avg}}^{*} \right)_{pl}$ is obtained in the same way as in previous sections of this paper and is shown in Fig. 5-23. Table 15 gives calculated value of $\left( \langle u_{p} \rangle_{\text{avg}}^{*} \right)_{pl}$ under the ideal plug flow inlet and ideal parabolic flow inlet conditions. Clearly, the maximum current density $i_{\text{max}}$ is proportional to $n$, $F$, $c$, $\left( \langle u_{p} \rangle_{\text{avg}}^{*} \right)_{pl}$, $t_{p}$ and $L$. The estimations of $i_{\text{max}}$ for a number of layers for the carbon fiber paper is given in Fig. 5-25. It can be seen that as the number of porous layer increases from 1 to 7, the maximum current density climbs from 403mA cm$^{-2}$ to 1301mA cm$^{-2}$ under the plug flow inlet condition. Results for one layer and three layers
of the carbon fiber paper compare favorably to the experimental results of Aaron et al. [21] as shown in Fig. 5-25.

Table 15 \( \langle u_p >_{avg}^* \rangle_{pl} \) for carbon fiber paper \((k=2.306 \times 10^{-10} \text{m}^2, \varepsilon=0.8)\), \(Re=91.5\)

<table>
<thead>
<tr>
<th>Number of porous layers</th>
<th>Ideal plug flow inlet ( (\langle u_p &gt;<em>{avg}^* \rangle</em>{pl} )</th>
<th>Ideal parabolic flow inlet ( (\langle u_p &gt;<em>{avg}^* \rangle</em>{pl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 6.126 \times 10^{-3} )</td>
<td>( 5.586 \times 10^{-3} )</td>
</tr>
<tr>
<td>2</td>
<td>( 4.384 \times 10^{-3} )</td>
<td>( 4.024 \times 10^{-3} )</td>
</tr>
<tr>
<td>3</td>
<td>( 3.753 \times 10^{-3} )</td>
<td>( 3.453 \times 10^{-3} )</td>
</tr>
<tr>
<td>4</td>
<td>( 3.393 \times 10^{-3} )</td>
<td>( 3.153 \times 10^{-3} )</td>
</tr>
<tr>
<td>5</td>
<td>( 3.153 \times 10^{-3} )</td>
<td>( 2.942 \times 10^{-3} )</td>
</tr>
<tr>
<td>6</td>
<td>( 2.972 \times 10^{-3} )</td>
<td>( 2.762 \times 10^{-3} )</td>
</tr>
<tr>
<td>7</td>
<td>( 2.822 \times 10^{-3} )</td>
<td>( 2.642 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

The estimated mean velocity in the flow channel \( u_{in} = 33.3 \text{cm s}^{-1} \) \((Re=91.5)\) leads to a value for \( (\langle u_p >_{avg}^* \rangle_{pl} \) of \( 6.13 \times 10^{-3} \) (single porous layer, \( t_p = 0.41 \text{mm}, t_p/t_{tot}=0.291 \)) and \( 3.75 \times 10^{-3} \) (three porous layers, \( t_p = 1.23 \text{mm}, t_p/t_{tot}=0.552 \) (see Fig. 5.23). The maximum current density is then estimated to be 403 mA cm\(^{-2}\) and 742 mA cm\(^{-2}\), respectively. The
estimated maximum current density is not so sensitive to the inlet boundary condition. Compared with the ideal parabolic inlet condition, the maximum current density is calculated to be slightly higher in the model with the ideal plug flow inlet. The numerical calculations are based on the assumptions made for property of electrolyte fluid, cell design parameters and estimated permeability of the porous electrode. The estimated maximum current density is actually very dependent on the permeability of the porous layer. These calculations use a $k=2.306 \times 10^{-10} \text{m}^2$, which may be large according to Weber et al. ($2 \times 10^{-11} \text{m}^2$). Using a smaller permeability will predict a much smaller amount of flow penetrating through the porous layer. However, the pressure drop along one channel and the along the adjacent returning flow channel will create a pressure gradient driving force that drives liquid to the adjacent flow channel through the porous layer. In this case, the distance between the adjacent flow channels is small (see Fig. 5-24 (d)), and the effect will be similar to our calculations except modified by a factor of about 10 (flow channel length divided by the average distance between the two flow channels, or 20/2). Consequently, the estimate of the maximum current density due to the bypass flow again gives a reasonable estimate of the maximum current density as compared to the experimentally reported value.
Figure 5-25 The relationship between the maximum current density possible from flow reactant supply and the number of porous layers for the carbon fiber paper ($\omega=20\text{ml min}^{-1}$, $c=1\text{M}$, $L=20\text{mm}$, $k=2.306\times10^{-10}\text{m}^3$), ideal plug flow inlet and parabolic flow inlet.
CHAPTER VI: Conclusions

A 2D macroscopic mathematical model is established to capture the dynamic flow patterns in RFBs represented by a single passage of a serpentine flow channel over a porous electrode. The non-dimensional average bulk flow velocity in the porous layer is found to decrease slightly from the developing to the fully developed flow region. The effects of entrance volumetric flow rate and permeability of foametal, carbon fiber paper or carbon felt and graphite felt porous samples give rise to a larger \( <u_p>_{\text{avg}} \) as \( u_{\text{in}} \) and \( k \) become larger.

However, \( <u_p>_{\text{avg}} \) shows a non-linear negative behavior as \( t_p \) ranges from 0.41mm to 2.87mm with fixed 1mm thickness of the flow channel and the non-dimensional parameters \( (<u_p>_{\text{avg}}^*)_{\text{pl}} \) shows a negative trend as \( t_p/t_{\text{tot}} \) climbs from 0.291 to 0.742 (the number of porous layer added from 1 to 7) under various Reynolds numbers ranging from 22.8 to 137.4 for the carbon fiber paper. Moreover, a model for describing the maximum current density is established which is related to number of electrons transferred during reactions, the Faraday constant, bulk concentration, the average velocity in porous layer and the geometric dimensions of the flow channel and the porous layer. For \( \text{Re}=91.5 \) (\( u_{\text{in}}=33.3 \text{cm s}^{-1} \)), \( (<u_p>_{\text{avg}}^*)_{\text{pl}} \) decreases from \( 6.13\times10^{-3} \) to \( 2.82\times10^{-3} \) and the maximum current density increases from 403mA cm\(^{-2}\) to 1301mA cm\(^{-2}\) as the number of carbon fiber layers is increased from 1 to 7. Predicted maximum current densities are compared with experimental results for 1 layer and 3 layers, with agreement well within the uncertainty in the measurements and values of the permeability of the porous layers (403mA cm\(^{-2}\) predicted vs. 400mA cm\(^{-2}\) measured for 1 layer, and 742mA cm\(^{-2}\) predicted vs. 750mA cm\(^{-2}\) measured for 3 layers)
CHAPTER VII: Future Work

(1) A 3D mathematical model for the “flow by” porous electrode with a serpentine flow channel with multiple flow passages in the RFBs needs to be developed. Compared with the 2D model with a single flow channel, 3D can more accurately represent the actual hydrodynamic and electro kinetics. The pressure drops from adjoining flow channels could drive more electrolyte into the porous layer and the possible turbulence around the corner of the flow channel could enhance the mass flow penetration in the porous layer and lead to a higher maximum current density. The effect of heat transfer should be taken into account although the variation of flow cell’s temperature is typically not large.

(2) More realistic models, 2D and 3D, for the porous solids, closer to the actual shapes, such as long irregular cylinders, random fiber structures are needed. The results of the physical models can be compared with the mathematical mode, such as that presented here.

(3) Work should continue on designing innovative flow cell configurations to obtain higher limiting current density, power density and efficiency with lower loss from ohmic resistance and concentration over-potential together with mass transport limitations.

(4) Carrying out more experiments on the type of electrolyte, materials of porous electrodes and ion selective membranes to motivate development new materials that would lead to high current density and reduce capital costs.

(5) Investigation of turbulent flow regimes at larger Reynolds number in the flow channel. In contrast to the low Reynolds number laminar flow (Re from 22.8 to 137.4 in this paper), turbulence flow would likely enhance mass flow in the porous layer.
(A.1) Maximum current density model

The maximum current density model derived in this studies is based on the mass balance and the Faraday’s law of Electrolysis

\[ m = \left( \frac{Q}{F} \right) \left( \frac{M}{n} \right) \]  

(A.1)

Where, \( m \) is the mass of flow reactants in the porous layer, \( Q \) is the total electric charge, \( F \) is the Faraday’s constant, \( M \) is the molar mass of flow reactants and \( n \) is the number of electrons involved in the chemical reactions. The total charge is related to current and time

\[ Q = It \]  

(A.2)

Where, \( I \)-current, \( t \)-time. Combination of equation (A.1) and equation (A.2) gives

\[ m = \left( \frac{It}{F} \right) \left( \frac{M}{n} \right) \]  

(A.3)

\[ m = \left( \frac{It}{nF} \right) \]  

(A.4)

Where, \( m = \frac{m}{M} \)

Switching equation (A.4) into molar mass flow rate
\[ \dot{m} = \left( \frac{1}{nF} \right) \]  

(A.5)

Where, \( \dot{m} = \frac{m}{t} \)

If the total flow reactants are consumed during the reactions, and the ion concentration reduces from \( c \) to zero

\[ \dot{m} = wt_p \left( \langle u_p \rangle_{avg} \right)_{pl} c \]  

(A.6)

Where, \( w \) is the width of the porous layer, \( t_p \) is the thickness of the porous layer, \( \langle u_p \rangle_{avg} \) is the average velocity throughout the porous layer, \( c \) is the ion concentration. The maximum current is estimated by equation (A.5) and equation (A.6)

\[ I_{max} = nFw t_p \left( \langle u_p \rangle_{avg} \right)_{pl} c \]  

(A.7)

Based on the contact area between the flow channel and the porous layer, the equation for predicting the maximum current density is obtained

\[ i_{max} = \frac{nFt_p \langle u_p \rangle_{avg}}{L} c \]  

(A.8)

Alternative form for equation (A.8)

\[ \frac{i_{max}}{u_{in}} = \frac{nFt_p \langle u_p \rangle_{avg}}{L} \cdot \frac{c}{L} \]  

(A.9)
Where, equation (A.9) is identical to equation (5.8). From equation (A.9) it’s clear to see that the value of the maximum current density is directly correlated to \( n, F, c, t_p, L, u_{in} \) and \((<u_p>_{avg})_{pl}^*\).
(A.2) No flow penetration-current density model

A no flow penetration model was put forward by Newman\[^{71}\] to predict the limiting current density for the electrolyte flowing through the flow channel and over the anode and cathode. It can be found in Newman’s model without considering the flow penetration into the porous electrode, the normal current density is equal to the average current density or limiting current density when $X^*$ is about 0.3. As $X^*$ increases from 0 to 1, the ratio between normal current density and the average current density gradually decreases.

Figure A-1 The relationship between the non-dimensional $i_n/i_{avg}$ or $i_n/i_{lim}$ with $X^*$ for the no flow penetration model
(A.3) Experimental data

The experimental data as shown in Fig. A-2 was observed by Aaron et al. [21]. The maximum current density for the single layer and three layers of carbon fiber paper from Fig. A-2 are compared with the predicted one from our numerical results.

Figure A-2 IR-free potential vs. current density from ref. [21]


