ASME Accepted Manuscript Repository

Institutional Repository Cover Sheet

First

Last

ASME Paper Title: A Three-dimensional Agglomerate Model of an Anion Exchange Membrane Fuel Cell

Authors: Machado BS; Chakraborty N; Mamlouk M; Das PK

ASME Journal Title: Journal of Electrochemical Energy Conversion and Storage

Volume/Issue 15(1) Date of Publication (VOR* Online) Oct 17, 2017

ASME Digital Collection URL: <http://electrochemical.asmedigitalcollection.asme.org/article.aspx?articleid=2659167>

DOI: <https://doi.org/10.1115/1.4037942>

*VOR (version of record)

Machado BS, Chakraborty N, Mamlouk M, Das PK.

**A Three-dimensional Agglomerate Model of an Anion Exchange Membrane
Fuel Cell.**

Journal of Electrochemical Energy Conversion and Storage 2017, 15(1),
011004.

Copyright:

© ASME 2017

DOI link to article:

<https://doi.org/10.1115/1.4037942>

Date deposited:

01/09/2017

Embargo release date:

17 April 2018

A Three-dimensional Agglomerate Model of an Anion Exchange Membrane Fuel Cell

Bruno S. Machado¹, Nilanjan Chakraborty¹, Mohamed Mamlouk², Prodip K. Das^{1,*}

¹School of Mechanical and Systems Engineering, Newcastle University, Newcastle-upon-Tyne, NE1 7RU, UK

²School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle-upon-Tyne, NE1 7RU, UK

Email: b.de-souza-machado1@newcastle.ac.uk (BSM); nilanjan.chakraborty@newcastle.ac.uk (NC)
mohamed.mamlouk@newcastle.ac.uk (MM); prodip.das@newcastle.ac.uk (PKD)

*Corresponding author. Tel: +44 191 208 6170

NOMENCLATURE

a_w	water activity	T	temperature, K
$a_{Pt/C}$	specific area, m^{-1}	T_0	operating temperature, K
A	active reaction area, m^2	$\vec{u}$	superficial velocity vector, $m\ s^{-1}$
C	molar concentration, $kmol\ m^{-3}$	V	Voltage, V
C_p	specific heat, $J\ kg^{-1}\ K^{-1}$	X	mole fraction
D_{ij}	Maxwell-Stefan diffusion coefficient matrix, $m^2\ s^{-1}$	Y	mass fraction
D	mass diffusivity, $m^2\ s^{-1}$	Greek letters	
E	effectiveness factor, total energy in the gaseous phase, J	α	transfer coefficient
EW	equivalent molecular weight of dry membrane, $kg\ kmol^{-1}$	δ	thickness, m
F	Faraday's constant, $C\ kmol^{-1}$	γ	water phase change rate, s^{-1}
h	latent heat, $J\ kg^{-1}$	ϵ	porosity
i	current density, $A\ m^{-2}$	ζ	water transfer rate, s^{-1}
j_0	exchange current density, $A\ m^{-2}$	η	overpotential, V
k	reaction rate coefficient, s^{-1} , thermal conductivity, $W\ m^{-1}\ kg^{-1}$	θ	contact angle, $^\circ$
k_p	permeability, m^2	κ	electrical conductivity, $S\ m^{-1}$
m	mass, kg	λ	membrane water content
L	largest dimension in the direction in question, m	$\emptyset$	Thiele's modulus, non-dimensional minimum cell distance
$\dot{m}$	mass flow rate, $kg\ s^{-1}$	μ	dynamic viscosity, $kg\ m^{-1}\ s^{-1}$
M	molecular weight, $kg\ kmol^{-1}$	ξ	stoichiometry ratio
$\vec{N}$	diffusion flux of species, $m^2\ s^{-1}$	ρ	density, $kg\ m^{-3}$
n_d	electro osmotic drag coefficient	σ	surface tension, $N\ m^{-1}$
p	pressure, Pa	ϕ	electronic potential
r	radius, m	Δ	cell size in the direction in question, m
R	universal gas constant, $J\ kmol^{-1}\ K^{-1}$	$\bar{\tau}$	viscous stress tensor, Pa
RH	relative humidity	Subscript and Superscript	
s	liquid water fraction	a	anode
S	source terms, entropy, $J\ kmol^{-1}\ K^{-1}$	agg	agglomerate
CL	catalyst layer	BP	bipolar plate

c	cathode, capillary
C	carbon
cell	cell
cond	condensation
d	dissolved
eff	effective
e	equilibrium
evap	evaporation
GDL	gas diffusion layer
g	gas phase
H_2	hydrogen
0	operating
l	liquid phase
mem	membrane
m	membrane phase
out	output
O_2	oxygen
ref	reference
rev	reversible
sat	saturation
s	solid phase
M	ionomer
i	species
v-l	vapour to liquid (vice-versa)
H_2O	water
w	water vapour phase

ABSTRACT

In this study, a three-dimensional agglomerate model of an anion exchange membrane fuel cell is proposed in order to analyse the influence of the composition on the catalyst layers (CLs) on overall fuel cell performance. Here, a detailed comparison between the agglomerate and a macro-homogeneous model is provided, elucidating the effects of the first implementation on the overall performance and the individual losses, the effects of operating temperature and inlet relative humidity on the cell performance, and the catalyst layer utilisation by the effectiveness factor. The results show that the macro-homogeneous model overestimates the cell performance compared to the agglomerate model due to the resistances associated with the species and ionic transports in the catalyst layers. Consequently the hydration is negatively affected, resulting in a higher Ohmic resistance. The activation overpotential is over-predicted by the macro-homogeneous model, as the agglomerate model relates the transportation resistances within the domain with the CL composition. Despite the higher utilisation in the anode CL, the cathode CL utilisation shows a significant drop near the membrane-CL interface due to a high current density and a low oxygen concentration. Additionally, the influences of operating temperature and relative humidity at the flow channel inlet have been analysed. Similar to the macro-homogeneous model, the overall cell performance of the agglomerate model is enhanced with increasing operating temperature due to the better electrochemical kinetics. However, as the relative humidity at the inlet is reduced, the overall performance of the cell deteriorates due to the poor hydration of the membrane.

Keywords: Anion exchange membrane fuel cell, agglomerate model, relative humidity, temperature.

1. INTRODUCTION

Fuel cells were traditionally used as power generators in space stations and satellites but their range of application has increased with time. For example, fuel cells are nowadays used in electric vehicles, electronic devices, and primary and backup power supply in remote zones. High efficiency and the lack of greenhouse gas emission are two of the main advantages of fuel cells in comparison to conventional fossil fuel engines. Among different types of fuel cells, polymer electrolyte fuel cell (PEFC) is one of the widely used types, which is characterized by a selective polymer membrane that allows either protons or anions to flow through it. The former is called proton exchange membrane (PEM) and the latter is called anion exchange membrane (AEM), and a schematic diagram representing both types is presented in Figure 1. The outputs of the overall electrochemical reaction that takes place in the catalyst layers include water molecules, heat and electrons [1]. Thus, the water management in polymer exchange membranes is crucial for proper functioning of fuel cells without compromising their performance. Several studies on PEM fuel cell reported the influences of both poorly and highly hydrated conditions on the overall performance of PEM fuel cells. For instance, Berg et al. [2] proposed a simplified two-dimensional model to evaluate the water management in PEM fuel cells. Oxygen transport in the ionomer was identified as a significant contributor to the mass losses in the fuel cell [2]. Das et al. [3, 4] evaluated the influences of wetting properties, flooding conditions, and geometric characteristics of the catalyst layer on the overall performance of PEM fuel cells. It was reported that the electro-osmotic drag and back diffusion are more likely to give rise to a flood condition than the water condensation within the catalyst and gas diffusion layer [3]. It was also reported that the wetting and geometric characteristics of catalyst layer have a significant influence on the liquid water transport, and thus on the overall cell performance [4]. Huo et al. [5] investigated the water management on the anode side for different operating conditions and reported that the influence of stoichiometry on the production of liquid water was not significant [5]. Nevertheless, the relative humidity at the inlet was directly associated with the water formation within catalyst and gas diffusion layers at the anode side [5]. Deng et al. [6] provided a multiphase transient investigation of the water formation and transport. It was shown that the time necessary to achieve a steady state solution under lower current density and operating temperature is smaller when compared to higher current density and temperature cases.

Nevertheless, this effect is observed to be insignificant under lower operating temperature conditions [6]. Later, a three-dimensional multiphase numerical model for AEM fuel cell was proposed by Jiao et al [7] and a single channel domain was considered. A parametric analysis was conducted and a relation between relative humidity and the current density was observed, although this effect was found to be less significant in the cases with higher relative humidity at both anode and cathode inlets [7]. An analytical model for AEM fuel cell was proposed by Jiao et al.[8], and their results indicated that the liquid humidification at the cathode inlet improves the fuel cell performance. Nevertheless under a cathode dry inlet and fixed stoichiometry ratio, the activation and Ohmic losses increase resulting in a lower overall fuel cell performance. Deng et al. [9] studied the interfacial effect on the AEM fuel cell performance. It was observed that inserting a micro-porous layer on cathode side has no significant influence as no liquid water is produced at the cathode side, nevertheless, when added in the anode side, it can enhance the water transportation from anode to cathode. Recently, we developed a three-dimensional numerical model for a typical AEM fuel cell to analyse the effects of flow direction, relative humidity at the inlet and temperature on the overall fuel cell performance [10]. It has been observed that the increases in operating temperature and relative humidity contribute to an increase in output current density. However, no significant influence of flow direction was observed for the set of parameters used. Moreover, the use of the macro-homogenous approach to model the catalyst-layers tends to overestimate the performance of AEM fuel cells, as the transports of species, electrons, ions and liquid water disregard the material composition of the catalyst layer. Numerical models have also been proposed for analysing the influences of materials composition on the overall performance of the fuel cells [11-14]. Sun et al. [11] proposed a two-dimensional agglomerate model to analyse the influences of structural parameters of the catalyst layer in PEM fuel cells. The numerical results suggested that the oxygen diffusion plays a role in the regions of high current density [11]. In addition to that, the transport of ions is shown to be as important as the oxygen diffusion in determining the overall fuel cell performance. Das et al. [14] proposed a three-dimensional agglomerate numerical model to investigate the activation overpotential in the cathode catalyst layer. The combination of lack of oxygen in the catalyst layer and the mitigation of void regions leads to high values of activation overpotential in the catalyst layer [14]. Results from an improved agglomerated model for the cathode

catalyst layer in PEM fuel cells [13] indicate that the drop in current density for lower cell voltages is directly associated with the oxygen transport through the cathode catalyst layer. In addition to the aforementioned agglomerate models, Yin [15] proposed a hybrid model with thin film/agglomerate characteristics and investigated the influence of oxygen diffusion within the polymer electrolyte. The analysis in Ref. [15] suggests that the electrolyte distribution plays a significant role in determining the overall performance of the fuel cell. Nevertheless, it is evident from the foregoing that agglomerate model was analysed for PEM fuel cells but a detailed species and charge transportation model in the catalyst layer for AEM fuel cells is yet to be reported in existing literature. The current analysis addresses the aforementioned gap in existing literature by developing a three-dimensional agglomerate model in order to address detailed transport of mass within the catalyst layer. Moreover, a comprehensive comparison between the overall performance of agglomerate and macro-homogeneous model [10] is made and the behaviours of the effectiveness factor, activation and concentration overpotential are also extensively analysed. Moreover, the effects of relative humidity and temperature on the overall performance of the fuel cell are discussed.

The rest of the paper will be organized as follows. The mathematical formulation and numerical implementation pertaining to this analysis will be presented in the next section. Following this, results will be presented and physical explanations for the observed behaviour will be provided. Finally, main findings will be summarized and conclusions will be drawn.

2. MATHEMATICAL BACKGROUND

2.1 Assumptions

A number of assumptions were made to simplify the computation and reduce the computational effort. These assumptions, however, do not compromise the physical characteristics of the AEM fuel cell. The assumptions made for the current computational analysis are summarized below:

- A three-dimensional single channel fuel cell is used to for the purpose of numerical simulations. As shown in Figure 2, the domain is composed of bipolar plate (BP), gas diffusion layer (GDL), catalyst layer (CL) and membrane.

- The ideal gas law is considered for the gaseous phase. In addition to that, the membrane is considered to be impenetrable by all species but the water.
- The water generated as a product of the electrochemical reaction is produced in the gaseous phase. Due to the operating conditions, water vapor might reach the saturation pressure and condense.
- Water can be transported through the membrane in a dissolved phase. The adsorption and desorption of water happen in the gaseous phase.
- The simulations were carried out in a steady state regime and body forces were neglected (e.g. gravity).
- The flow in the channel is assumed to be laminar because the Reynolds number in a typical case was found to be of the order of 100.

2.2 Mathematical framework

2.2.1 Transport equations of gas mixture

The conservation of mass and species is obtained by associating the Darcy's Law and the Maxwell-Stefan equation. Thus, mass and species conservation equations can be described as, respectively:

$$-\nabla \cdot (\rho^g \vec{u}^g) = -\nabla \cdot \left(\rho^g \frac{k_p}{\mu^g} \nabla p \right) = S_{mass} \quad (1)$$

$$-\rho^g \vec{u}^g \cdot \nabla Y_i^g - \nabla \cdot \left[-\rho^g \sum_{j=1}^N (1-s) D_{ij} \left(\nabla X_j^g - Y_i^g \right) \frac{\nabla p}{p} \right] = S_i \quad (2)$$

where ρ^g is the gas density, k_p is the permeability of the porous media, μ^g is the viscosity of the gas mixture, p is the pressure, $\vec{u}^g$ is the gaseous phase superficial velocity, Y_i^g is the mass fraction of the i^{th} species, s is the liquid water volume fraction, D_{ij} is the binary diffusion coefficient and X_j^g is the molar fraction of the j^{th} species. The expressions needed to compute the binary diffusion coefficients and also the Lennard-Jones parameters are obtained from Xing et al. [13]. The source terms S_{mass} and S_i are the mass and species source terms, respectively, and are presented in Table 1.

In addition to that, the Navier-Stokes equation is used to describe the momentum transport as follows:

$$\rho^g (\vec{u}^g \cdot \nabla \vec{u}^g) + \frac{\mu^g}{k_p} \vec{u}^g = -\nabla p + \nabla \cdot (\bar{\tau}) \quad (3)$$

where $\bar{\tau}$ is the viscous stress tensor.

2.2.1.1 Catalyst layer composition

In this study, a three-dimensional spherical agglomerate model is proposed in order to discretise the domain of the catalyst layer. Therefore, the volume fractions of evenly distributed spheres composed of platinum dispersed carbon ($L_{Pt/C}$), ionomer (L_M) and the pores (ϵ_{CL}) are considered for describing the catalyst layer. A two-dimensional schematic representation of one such sphere is presented in Figure 3, where δ is the thickness of the ionomer film covering the Pt/C agglomerate, r_{Pt} is the radius of an individual Pt particle, $C_{i,g/M}$ represents the concentration of the i^{th} species at the gas and ionomer interface and $C_{i,M/s}$ represents the concentration of the i^{th} species at the ionomer and solid particle interface. Thus, the catalyst composition in terms of the volume fractions can be expressed as:

$$L_{Pt/C} + L_M + \epsilon_{CL} = 1 \quad (4)$$

The volume fraction of Pt/C in the catalyst layer is given by [16]:

$$L_{Pt/C} = \left(\frac{1}{\rho_{Pt}} + \frac{1-\%Pt}{\%Pt\rho_C} \right) \frac{m_{Pt}}{\delta_{CL}} \quad (5)$$

$$\%Pt = \frac{m_{Pt}}{m_{Pt} + m_C} \quad (6)$$

where m_{Pt} and m_C are the mass of Pt and C per unit of geometric area, respectively. Here, instead of defining the catalyst layer with respect of the geometrical area, an effective specific area per unit catalyst layer volume is used. Thus, the effective specific platinum surface area per unit catalyst layer volume is defined as:

$$a_{Pt,cl}^{eff} = \frac{3L_{Pt/C} m_{Pt}}{r_{Pt}\rho_{Pt}\delta_{CL}} \quad (7)$$

where the subscript cl corresponds to either anode (a) or cathode (c) side.

2.2.2 Current distribution

The current distributions of electronic and ionic potential are described by the Ohm's law, and are presented as:

$$-\nabla \cdot (\kappa_s^{eff} \nabla \phi_s) = S_s \quad (8)$$

$$-\nabla \cdot (\kappa_m^{eff} \nabla \phi_m) = S_m \quad (9)$$

where ϕ_s and ϕ_m are the electronic and ionic potential, respectively, κ_s^{eff} and κ_m^{eff} are the effective conductivity of electrons and ions, respectively; S_s and S_m are the source term for the electronic and ionic potential conservation equations, respectively. As the electronic and ionic diffusion coefficients are dependent on the catalyst layer composition, they have to be corrected accordingly. One can correct the bulk diffusion coefficients of electrons and ions using the Bruggeman approximation as [17]:

$$\kappa_s^{eff} = (L_{Pt/C})^{1.5} \kappa_s \quad (10)$$

$$\kappa_m^{eff} = L_M^{1.5} \kappa_m \quad (11)$$

where κ_s and κ_m are the electronic and ionic conductivity, respectively. It has been reported that the ionic conductivity is dependent on the temperature and water activity in the vapour phase [18]. Thus, the following expressions are used to define the ionic conductivity [7]:

$$\begin{aligned} a_w = & 0.8118 - 2.296 \times 10^{-3} T_0 + (5.815 \times 10^{-3} T_0 - 2.005) \lambda - (2.977 \times 10^{-3} T_0 - \\ & 1.046) \lambda^2 + (4.825 \times 10^{-4} T_0 - 0.1676) \lambda^3 - (3.179 \times 10^{-5} T_0 - 0.01094) \lambda^4 + \\ & (7.427 \times 10^{-7} T_0 - 2.539 \times 10^{-4}) \lambda^5 \end{aligned} \quad (12)$$

$$\begin{aligned} \kappa_m = & 0.1334 - 3.882 \times 10^{-4} T_0 + (0.01148 T_0 - 3.909) a_w - (0.06690 T_0 - 23.01) a_w^2 + \\ & (0.1227 T_0 - 42.61) a_w^3 - (0.06021 T_0 - 21.80) a_w^4 \end{aligned} \quad (13)$$

where a_w is the water activity in the vapour phase and T_0 is the operating temperature. The electronic conductivity is considered to be constant and it is provided in Table 2.

2.2.3 Electrochemical reaction on the catalyst surface

Generally, in the macro-homogeneous model, the local volumetric reaction rate at anode and cathode catalyst layers is described by the Butler-Volmer equation [10]. Nevertheless, Sun et al. [11] adopted the Butler-Volmer equation to take into account the effects of porosity within the catalyst layer and the resistance due to the agglomerate film surrounding the agglomerate. Thus, the electrochemical reaction in the anode and cathode side can be described as [12]:

$$i_a = 2F \left(\frac{p_{H_2}}{H_{H_2}} \right)^{0.5} \left[\frac{1}{E_{r,a} k_a} + \frac{(r_{agg} + \delta_{agg}) \delta_{agg}}{a_{agg} r_{agg} D_{H_2-M}} \right]^{-1} \quad (\text{for anode}) \quad (14)$$

$$i_c = 4F \frac{p_{O_2}}{H_{O_2}} \left[\frac{1}{E_{r,c} k_c} + \frac{(r_{agg} + \delta_{agg}) \delta_{agg}}{a_{agg} r_{agg} D_{O_2-M}} \right]^{-1} \quad (\text{for cathode}) \quad (15)$$

where F is the Faraday constant (96487000 C/kmol); H_{H_2} and H_{O_2} are the Henry's constant for hydrogen and oxygen, respectively; p_{H_2} and p_{O_2} are the partial pressure of hydrogen and oxygen, respectively; D_{H_2-M} and D_{O_2-M} are the hydrogen and oxygen diffusion coefficients through the ionomer; r_{agg} and a_{agg} are the radius of the agglomerate and the effective specific agglomerate surface area. The effectiveness factor, E_r , measures the utilisation of the catalyst layer and is defined as:

$$E_{r,cl} = \frac{1}{\phi_L} \left(\frac{1}{\tanh(3\phi_L)} - \frac{1}{3\phi_L} \right) \quad (16)$$

where ϕ_L is a dimensional group known as Thiele's modulus and is given by:

$$\phi_{L,cl} = \frac{r_{agg}}{3} \sqrt{\frac{k_{cl}}{D_{eff,cl}}} \quad (17)$$

where D_{eff} is the effective diffusion of hydrogen and oxygen in the ionomer, and is expressed as, respectively,

$$D_{eff,a} = D_{H_2-M} L_M^{1.5} \quad (\text{for anode}) \quad (18)$$

$$D_{eff,c} = D_{O_2-M} L_M^{1.5} \quad (\text{for cathode}) \quad (19)$$

The hydrogen and oxygen diffusion coefficients through the ionomer have been addressed in this work.

The reaction rate coefficient, k_{cl} , is expressed as [12]

$$k_a = \left(\frac{a_{Pt,a}^{eff}}{2F(1-\epsilon_{CL})} \right) \left[\frac{j_{0,a}^{ref}}{(C_{H_2}^{ref})^{0.5}} \right] \left[\exp\left(\frac{n\alpha_a F}{RT} \eta\right) - \exp\left(\frac{n(1-\alpha_a)F}{RT} \eta\right) \right] \quad (20)$$

$$k_c = \left(\frac{a_{Pt,c}^{eff}}{4F(1-\epsilon_{CL})} \right) \left[\frac{j_{0,c}^{ref}}{C_{O_2}^{ref}} \right] \left[\exp\left(\frac{n\alpha_c F}{RT} \eta\right) - \exp\left(\frac{n(1-\alpha_c)F}{RT} \eta\right) \right] \quad (21)$$

where $C_{H_2}^{ref}$ and $C_{O_2}^{ref}$ are the reference molar concentration of hydrogen and oxygen, respectively; $j_{0,a}^{ref}$ and $j_{0,c}^{ref}$ are the exchange current densities at the anode and cathode side, respectively; α_a and α_c are the anodic and cathodic charge transfer coefficients, respectively; n is the number of electrons simultaneously release or uptake; R is the universal gas constant (8314 J/kmolK); T is the absolute temperature in K and η is the overpotential. The overpotential, η , is defined as follows:

$$\eta = \phi_s - \phi_m \quad (22)$$

The electrochemical kinetics parameters used to perform the numerical simulation are covered in Table 3 according to Ref. [19].

2.2.4 Species transportation in the catalyst layer

The transportation of species within the catalyst layer is significantly affected by the medium. As shown in Figure 1, the agglomerate particle is composed of three different volume fractions ($L_{Pt/C}$, L_M , ϵ_{CL}). Thus, as for the species diffusion in the void space, Eq. 2 is used to govern the process through the porous structure. Nevertheless, due to the lack of experimental parameters correlating the diffusion coefficients for the commercial Tokuyama A201 membrane, the values of diffusion coefficient used in the present work correspond to Nafion™. Parthasarathy et al. [20] investigated the diffusion of oxygen in Nafion™. The oxygen diffusivity is dependent on temperature and, for a 100% relative humidity case, it is expressed as [11]:

$$D_{O_2-M} = 0.00000438 \exp\left(-\frac{E_d}{RT}\right) \quad (23)$$

where E_d is the activation energy for diffusion and has been reported to be 25000kJ/kmol [11]. The hydrogen diffusion coefficient in Nafion™ has been correlated with temperature as [21] as:

$$D_{H_2-M} = 0.00000041 \exp\left(-\frac{2602.0}{T}\right) \quad (24)$$

2.2.5 Membrane water content

The conditions at which the fuel cell is supposed to operate are favorable to the sorption of water by the membrane. In addition to that, the transport of anions through the membrane is responsible for dragging water through it. Thus, the membrane water content conservation equation is given as [22]:

$$-\nabla \cdot (D_d^{\text{eff}} \nabla \lambda) + \nabla \cdot \left(\frac{EW}{\rho_{mem}} \frac{n_d}{F} \vec{j}_m \right) = S_d \quad (25)$$

where D_d is the diffusivity of the membrane water content, EW is the equivalent molecular weight of the membrane in a dry condition, ρ_{mem} is the membrane density. The membrane water content can also be described with respect to the dissolved water concentration as:

$$\lambda = \frac{EW}{\rho_{mem}} C_d \quad (26)$$

where C_d is the dissolved water molar concentration. For the catalyst layer, the water diffusion coefficient of the membrane was corrected by the ionomer content in the catalyst layer as:

$$D_d^{\text{eff}} = L_M^{1.5} D_d \quad (27)$$

where D_d is the diffusion coefficient of water membrane content, which is expressed as [5]:

$$D_d = \begin{cases} (0.0051\lambda T_0 - 1.44\lambda) \times 10^{-10} & 0.0 \leq \lambda \leq 14.0 \\ \left[(-23.2404 + 4.513\lambda - 0.28926\lambda^2 + 0.006131\lambda^3)(T_0 - 303.15) \right. \\ \quad \left. - 79.826 + 17.928\lambda - 1.3329\lambda^2 + 0.03337\lambda^3 \right] \times 10^{-10} & 14.0 < \lambda \leq 19.0 \\ [(-41.916 + 0.00613\lambda^3)(T_0 - 303.15) + 8.5139] \times 10^{-10} & \lambda > 19.0 \end{cases} \quad (28)$$

The electro-osmotic drag coefficient, n_d , is expressed as [23]:

$$n_d = \frac{2.5}{22} \lambda \quad (29)$$

The sorption and desorption processes are governed by the equilibrium approach proposed by Berg et al. [2]. Thus, the use of membrane water content in an equilibrium hydration state, λ_e , is necessary and it can be computed as [7]:

$$\lambda_e = \begin{cases} (-0.605a^3 + 0.85a^2 - 0.205a + 0.153)(T_0 - 313.15) + 39.0a^3 - 47.7a^2 + 23.4a + 0.117 & 0 \leq a \leq 1.0 \\ (-0.00265a + 0.05795)(T_0 - 313.15) + 1.5915(a - 1) + 14.817 & 1.0 < a \leq 3.0 \end{cases} \quad (30)$$

where the water activity, a , is a function of the water vapour partial pressure and the liquid water saturation, and it is defined as:

$$a = \frac{X_{H_2O} p_g}{p_{sat}} + 2s \quad (31)$$

2.2.6 Liquid water fraction

By applying a volume average approach to the continuity equation for the liquid water fraction and also using the Darcy law, the liquid water conservation equation can be written as [22]:

$$\nabla \cdot \left(-\frac{\rho_l s^3}{\mu_l} \frac{dP_c}{ds} \right) \nabla s + \nabla \cdot \frac{\rho_l \mu_g s^3}{\mu_l (1-s)^3} \vec{u}_g = S_l \quad (32)$$

where ρ_l is the liquid water density, μ_l and μ_g are the dynamic viscosity of liquid water and water vapour, respectively; s is the volume fraction of liquid water and the S_l is the liquid water source term and is presented at Table 1. The capillary pressure, P_c , according to the Leverett-J function [3, 24], is expressed as:

$$P_c = \begin{cases} \sigma \cos \theta \left(\frac{\epsilon}{K_0} \right)^{0.5} [1.42(1-s) - 2.12(1-s)^2 + 1.26(1-s)^3] & \text{if } \theta \leq 90^\circ \\ \sigma \cos \theta \left(\frac{\epsilon}{K_0} \right)^{0.5} [1.42s - 2.12s^2 + 1.26s^3] & \text{if } \theta > 90^\circ \end{cases} \quad (33)$$

where σ is the surface tension coefficient and θ is the contact angle.

Due to the temperature and pressure in the anode catalyst and gas diffusion layers, water vapor might reach a saturated condition and condensation may take place. The vapor saturation pressure is obtained using the following empirical expression [23]:

$$\log_{10} \left(\frac{p_{sat}}{101325} \right) = -2.1794 + 0.02953(T - 273.15) - 9.1837 \times 10^{-5}(T - 273.15)^2 + 1.4454 \times 10^{-7}(T - 273.15)^3 \quad (34)$$

2.2.7 Energy equation

A non-isothermal approach is considered in this study. Thus, the energy equation of a multi-phase flow in porous media is presented as:

$$\nabla \cdot (\vec{u}_g (\rho_g E_g + p_g)) = \nabla \cdot (k^{eff} \nabla T - (\sum_i h_i \vec{N}_i) + (\vec{\tau} \cdot \vec{u}_g)) + S_E \quad (35)$$

where k^{eff} is the effective conductivity, E_g is the total energy in the gaseous phase, h_i is the sensible enthalpy for the i^{th} species, $\vec{N}_i$ is the diffusion flux of the i^{th} species. The source of heat, S_E , is presented in Table 1. There, the different sources of heat are presented: reversible heat, the irreversible heat, the Ohmic heat and the latent heat due to phase change.

2.2.8 Boundary conditions

The species concentrations at the inlet of anode and cathode flow channel are defined as:

$$C_{H_2} = \frac{(p_a - RH \ p_{sat})}{RT_0} \quad (36)$$

$$C_{O_2} = \frac{0.21(p_c - RH \ p_{sat})}{RT_0} \quad (37)$$

where p_a and p_c are the inlet pressure at the anode and cathode, RH is the relativity humidity at the inlet and the operating temperature, T_0 , is also specified at both anode and cathode inlets. These are used to compute the mass flow rates at the anode and cathode sides, respectively, as:

$$\dot{m}_a = \frac{\rho_g^a \xi_a I_{ref} A}{2FC_{H_2}} \quad (38)$$

$$\dot{m}_c = \frac{\rho_g^c \xi_c I_{ref} A}{4FC_{O_2}} \quad (39)$$

where ξ_a and ξ_c are the stoichiometry ratios of anode and cathode, respectively; I_{ref} is the reference current density; A is the active reaction area; ρ_g^a and ρ_g^c are the densities of the gas mixture at the anode and cathode inlets, respectively.

In this study, the boundary condition for the electronic potential was considered to be the same as suggested by Hao *et al.* [22]. Thus, the electronic potential boundary conditions at the top and bottom of anode and cathode electrodes are:

$$\phi_s^a = V_{rev} - V_{out} \text{ (for anode)} \quad (40)$$

$$\phi_s^c = 0.0 \text{ (for cathode)} \quad (41)$$

where V_{rev} is the theoretical reversible voltage [10] and V_{out} is the output voltage.

The Neumann condition is applied for all other boundary conditions, which is given by:

$$\frac{\partial \varphi}{\partial n} = 0.0 \quad (42)$$

where φ is the relevant primitive variable.

2.2.9 Computational domain

A straight channel half-channel is considered to be the computational domain and its schematic representation is shown in Figure 2. The half-cell is considered for the computational economy. The physical dimensions and properties are listed in Table 2 and Table 4 [7, 19], respectively.

2.2.10 Numerical procedure

In order to solve the governing equations, a finite volume method based commercial software ANSYS FLUENT was used. All the governing equations, including the scalar transport equations, implemented through the use of user define functions (UDF), were solved in a coupled manner. The SIMPLE algorithm was used to link velocity and pressure. Second order central difference and upwind schemes were used to solve the diffusive and convective terms, respectively. With the respect of the spatial discretisation of the computational domain, a mesh independence test was carried out. The approach used in our earlier study [10] to compute the error associated with the mesh refinement is utilised in this analysis. Here, mesh M5 is used and, as one can see from Table 5, the total error associated with the spatial discretisation is 2%. Due to the wide range of operating parameters, structural composition of the fuel cell components and the lack of information regarding some of the transportation characteristics related to the membrane Tokuyama A201, a direct comparison with a single experimental dataset might not be sufficient. Therefore, the present numerical model is validated by comparing the polarisation

curve produced with the experimental results from different authors [25-27]. As one can see in Figure 4, the current model shows a good qualitative agreement with the different experimental results using the Tokuyama A201 membrane. Further discussion regarding the parameters used to produce the polarisation curve is presented in the next section.

3. RESULTS AND DISCUSSION

The three-dimensional agglomerate model for a multiphase flow for a typical AEM fuel cell is developed and used in this work to analyse the influences of species transport within the catalyst layers. A summary of the source terms for the continuity, momentum, species, electronic potential, ionic potential, membrane water content, liquid water, and energy conservation equations is presented in Table 6. The operating parameters used to perform these simulations are presented in Table 7. A detailed analysis of the influences of species transport on the overall fuel cell performance is provided in the next subsections.

3.1 Overall performance

Generally, the performance of fuel cells is assessed by comparing polarisation curves. Thus, the overall performance of the AEM fuel cell for the current agglomerate model data is compared with the several experimental data as well as with the previously developed macro-homogeneous model [10], as shown in Figure 4. In order to compare between macro-homogeneous and agglomerate models, all the parameters are kept the same for both models (see Table 2 and Table 4). It can be seen from Figure 4 that both macro-homogeneous and agglomerate numerical models are capable of capturing the trend of the experimental results. As the macro-homogeneous model does not account for subtle transport characteristics and dependencies on catalyst layer composition, it overestimates the fuel cell performance in comparison to the agglomerate model. An overview of the losses for both agglomerate and macro-homogeneous models in the case of 0.5 V output voltage is shown in Figure 5. It can be seen from Eq. 22 that the overpotential is defined as the difference between electronic and ionic potentials. No significant difference is observed in the values of electronic potentials between the agglomerate and macro-homogeneous models. Nevertheless, the ionic potential for the agglomerate model is observed to be smaller than the ionic potential for the macro-homogeneous model. This is directly associated

with the hydration state of the membrane. As the reaction rate for the agglomerate model is smaller than the macro-homogeneous model, less water is produced as a product of the electrochemical reaction, which decreases the amount of water sorption in the interface of anode catalyst layer and membrane. Moreover, as the flux of ions from the anode to cathode side decreases, less water is dragged due to the ions transport, which supports the less hydrated state in the agglomerate model in comparison to the macro-homogeneous model. For the current analysis, about 70% of the losses are related to Ohmic losses as the ionic conductivity of the current membrane is over one order of magnitude lower than an ordinary Nafion membrane. The activation and concentration losses in the agglomerate model are responsible for the remaining 30%. Further explanation regarding the impact of the extra resistances due to the agglomerate model in the activation and concentration losses are provided in the following sub-sections.

3.2 Concentration overpotential

In the catalyst layer, momentum and species conservation equations are used to govern the transport of species within the computational domain. Although the use of the aforementioned equations in a macro-homogeneous model provides a qualitatively correct representation of the main physics of the fuel cell, it is necessary to add corrections to the electrochemical kinetics in order to account for all the different transport coefficients and dependencies on the catalyst layer composition. As shown in Figure 3, the cathode and anode catalyst layers are considered to be made up of spherical Pt/C agglomerate with void regions covered by the ionomer according to the agglomerate model. As the ionomer layer covers the spherical agglomerate, an extra resistance is added to the transport model, and thus the concentration loss is expected to increase. It can be seen from Figure 6 that the concentration loss profiles at the middle plane section at the cathode CL for the macro-homogeneous and agglomerate models are significantly different. As the partial pressure of oxygen diminishes near the catalyst/membrane interface, especially under the bipolar plate region, the rate of oxygen crossing the ionomer cover around the particle sphere decreases in the context of the agglomerate model. The starvation of oxygen in contact with the Pt/C agglomerate is responsible for the mass transfer associated losses, which reduces the overall performance of the fuel cell. From the combination of Eq. 15 and Eq. 21, one can see that the ratio of reference and current molar concentration is impacting on the concentration loss.

Nevertheless, the reference values of the catalyst layer used in this study were measured at higher pressure, thus, under the current operating conditions, the overpotential benefits from the ratio of reference and current molar concentration. Regarding the concentration loss on the anode side, the faster diffusion of the hydrogen in the ionomer compared to the oxygen results in a marginal change in the concentration loss between agglomerate and macro-homogeneous models, and thus will not be presented here for the sake of conciseness.

3.3 Activation overpotential

As the effect of the activation potential is pronounced under lower output voltage conditions, this aspect will be discussed for the 0.9V output case. The contours of the activation loss in the cathode catalyst layer for both agglomerate and macro-homogeneous models are presented in Figure 7. It can be seen from Figure 7 that the contribution of the activation loss to the total overpotential in the cathode catalyst layer is greater in the agglomerate model than in the macro-homogeneous model, which leads to an overestimation of the fuel cell performance by the macro-homogeneous model. This loss in the agglomerate model arises due to the usage of an effective specific platinum surface area per unit catalyst layer volume because the composition and physical dimensions of the catalyst layer have direct impacts on the activation potential. From Eq. 5 and Eq. 7, one can see that increasing the amount of Pt/C deposition in the catalyst layer is beneficial to the activation potential. Nevertheless, the void volume fraction in the catalyst layer is directly affected by the increase of Pt/C deposition, which also contributes to the starvation of the species in the reactive sites.

3.4 Effectiveness factor

The implementation of the agglomerate model introduces the effectiveness factor for the catalyst layer, which is expressed by Eq. 16, and it quantifies the utilisation of the catalyst layer through the ratio of species diffusion in the ionomer and electrochemical reaction rate constant. It is worth mentioning that the unity effectiveness factor does not mean a high reaction rate, but a more uniform reaction through the catalyst layer site. The effectiveness factor for the anode and cathode catalyst layers is presented in Figure 8. The effectiveness factor in the anode side does not vary significantly through the length of the catalyst layer, which implies that the utilisation of the catalyst layer at the anode side is mostly even. Nevertheless, despite the faster hydrogen diffusion, one can observe a drop, although not significantly,

in the region closer to the membrane and catalyst layer interface. As seen in the previous section, the higher overpotential is located at the interface of membrane and catalyst layer. Thus, the higher demand for hydrogen and the slightly short supply of it causes the drop in the effectiveness factor. Nonetheless, on the cathode side, the effectiveness factor shows significantly drop as the membrane interface is approached. Here several factors need to be taken into consideration for explaining this drop. The diffusion of oxygen is slower than hydrogen diffusion. As the air is supplied with humidified state, oxygen has to compete with water molecules to diffuse through the pores of the catalyst layer. This resistance causes the lack of oxygen near the interface of the catalyst layer with the membrane, which further reduces the utilisation of the catalyst in that area. Another important aspect is that the reaction rate variation through the length of the catalyst layer. For the case analysed here, a wide range of overpotential is observed, which results in a considerable variation of the reaction rate. Therefore, the utilisation of the catalyst layer on the cathode side is compromised.

3.5 Effect of temperature and relative humidity

In addition to the comparison between macro-homogeneous and agglomerate models from the overpotential and loss perspective, the effects of operating temperature and relative humidity at the inlet channels on the overall performance are also analysed. The effect of the temperature can be seen in Figure 9. As previously observed in our macro-homogeneous model, the rise in the operating temperature of the fuel cell also resulted in an enhancement of the overall performance of the agglomerate model. This is mainly associated with the enhancement of the electrochemical kinetics and ionic diffusion facilitated at high temperatures. With the respect of the effect of the relative humidity, as presented in Figure 10, the overall fuel cell performance is negatively affected in comparison to the fully humidified operation condition for operating conditions with small values of relative humidity. As the presence of water vapor in the catalyst layer is scarce, the humidification of the membrane is compromised for small values of relative humidity. Therefore, the ion transportation reduces and the Ohmic loss increases for small values of relative humidity, resulting in a deteriorated overall performance of the fuel cell.

4. CONCLUSIONS

A three-dimensional agglomerate model has been developed to analyse the performance of a generic anion exchange membrane fuel cell. Here, a detailed comparison between the proposed agglomerate model and a previously developed macro-homogeneous model is presented. On the aspect of overall performance, the macro-homogeneous model overestimates the performance of the fuel cell when compared to the agglomerate model. This is mainly attributed to the subtle transport phenomena, which is not considered in the macro-homogeneous model. The lower reaction rate also affects the membrane hydration as less water is produced and dragged due to the transportation of ions through the membrane. Thus, the Ohmic resistance is partially responsible for the deterioration of the overall performance of the fuel cell according to the agglomerate model.

The activation and concentration overpotentials of the agglomerate and macro-homogeneous models are compared. The concentration overpotential profile in the cathode catalyst layer differs significantly between the macro-homogeneous and agglomerate models because the agglomerate model introduces resistances due to the transportation through the ionomer. Nevertheless, the faster diffusion of hydrogen in the ionomer did not significantly affect the concentration overpotential on the anode side. With respect of the activation overpotential, the agglomerate model is overpredicted by the macro-homogeneous model, resulting in an overestimation of the activation overpotential of the macro-homogeneous model. This is directly associated with the consideration of the effective specific platinum surface area per unit catalyst layer volume because the amount of Pt/ C volume fraction and platinum loading have a direct impact on the reaction rate. The distribution of effectiveness factor of the catalyst layer has been analysed in detail in the context of the agglomerate model. The anode effectiveness factor does not show any significant variation, which implies uniform utilisation of the catalyst layer. However, the utilisation of the cathode catalyst layer is compromised by the slower diffusion rate of oxygen and the cathode catalyst layer also exhibits a significant variation of the reaction rate through the catalyst layer length.

The influences of the relative humidity and temperature on the overall performance of the fuel cell in the context of the agglomerate model have been found to be qualitatively similar to those obtained from

the macro-homogeneous model. An increase in the temperature positively affects the overall performance mainly due to the enhancement of the electrochemical kinetics. By contrast, the supply of less humidified gas in at the inlet results in a less favorable condition for the anion transportation, which in turn deteriorates the overall performance of the fuel cell.

ACKNOWLEDGEMENTS

The financial support of CAPES (the Science without Borders Project) through the grant n. BEX / 13011-13-8 is gratefully acknowledged.

REFERENCES

- [1] Weber, A. Z., Borup, R. L., Darling, R. M., Das, P. K., Dursch, T. J., Gu, W. B., Harvey, D., Kusoglu, A., Litster, S., Mench, M. M., Mukundan, R., Owejan, J. P., Pharoah, J. G., Secanell, M., and Zenyuk, I. V., 2014, "A Critical Review of Modeling Transport Phenomena in Polymer-Electrolyte Fuel Cells," *J Electrochem Soc*, 161(12), pp. F1254-F1299.
- [2] Berg, P., Promislow, K., St Pierre, J., Stumper, J., and Wetton, B., 2004, "Water management in PEM fuel cells," *J Electrochem Soc*, 151(3), pp. A341-A353.
- [3] Das, P. K., Li, X., and Liu, Z. S., 2010, "Analysis of liquid water transport in cathode catalyst layer of PEM fuel cells," *Int J Hydrogen Energ*, 35(6), pp. 2403-2416.
- [4] Das, P. K., Li, X., Xie, Z., and Liu, Z. S., 2011, "Effects of catalyst layer structure and wettability on liquid water transport in polymer electrolyte membrane fuel cell," *Int J Energ Res*, 35(15), pp. 1325-1339.
- [5] Huo, S., Deng, H., Chang, Y. F., and Jiao, K., 2012, "Water management in alkaline anion exchange membrane fuel cell anode," *Int J Hydrogen Energ*, 37(23), pp. 18389-18402.
- [6] Deng, H., Huo, S., Chang, Y. F., Zhou, Y. B., and Jiao, K., 2013, "Transient analysis of alkaline anion exchange membrane fuel cell anode," *Int J Hydrogen Energ*, 38(15), pp. 6509-6525.
- [7] Jiao, K., He, P., Du, Q., and Yin, Y., 2014, "Three-dimensional multiphase modeling of alkaline anion exchange membrane fuel cell," *Int J Hydrogen Energ*, 39(11), pp. 5981-5995.
- [8] Jiao, K., Huo, S., Zu, M., Jiao, D. K., Chen, J. X., and Du, Q., 2015, "An analytical model for hydrogen alkaline anion exchange membrane fuel cell," *Int J Hydrogen Energ*, 40(8), pp. 3300-3312.
- [9] Deng, H., Wang, D. W., Xie, X., Zhou, Y. B., Yin, Y., Du, Q., and Jiao, K., 2016, "Modeling of hydrogen alkaline membrane fuel cell with interfacial effect and water management optimization," *Renew Energ*, 91, pp. 166-177.
- [10] Machado, B. S., Chakraborty, N., and Das, P. K., 2017, "Influences of flow direction, temperature and relative humidity on the performance of a representative anion exchange membrane fuel cell: A computational analysis," *Int J Hydrogen Energ*, 42(9), pp. 6310–6323.

- [11] Sun, W., Peppley, B. A., and Karan, K., 2005, "An improved two-dimensional agglomerate cathode model to study the influence of catalyst layer structural parameters," *Electrochim Acta*, 50(16-17), pp. 3359-3374.
- [12] Xing, L., Liu, X. T., Alaje, T., Kumar, R., Mamlouk, M., and Scott, K., 2014, "A two-phase flow and non-isothermal agglomerate model for a proton exchange membrane (PEM) fuel cell," *Energy*, 73, pp. 618-634.
- [13] Xing, L., Mamlouk, M., and Scott, K., 2013, "A two dimensional agglomerate model for a proton exchange membrane fuel cell," *Energy*, 61, pp. 196-210.
- [14] Das, P. K., Li, X., and Liu, Z. S., 2008, "A three-dimensional agglomerate model for the cathode catalyst layer of PEM fuel cells," *J Power Sources*, 179(1), pp. 186-199.
- [15] Yin, K. M., 2007, "A thin-film/agglomerate model of a proton-exchange-membrane fuel cell cathode catalyst layer with consideration of solid-polymer-electrolyte distribution," *J Appl Electrochem*, 37(8), pp. 971-982.
- [16] Das, P. K., Li, X., and Liu, Z. S., 2007, "Analytical approach to polymer electrolyte membrane fuel cell performance and optimization," *J Electroanal Chem*, 604(2), pp. 72-90.
- [17] Das, P. K., Li, X., and Liu, Z. S., 2010, "Effective transport coefficients in PEM fuel cell catalyst and gas diffusion layers: Beyond Bruggeman approximation," *Appl. Energ.*, 87(9), pp. 2785-2796.
- [18] Siegel, C., 2008, "Review of computational heat and mass transfer modeling in polymer-electrolyte-membrane (PEM) fuel cells," *Energy*, 33(9), pp. 1331-1352.
- [19] Liu, X. L., Lou, G. F., and Wen, Z., 2010, "Three-dimensional two-phase flow model of proton exchange membrane fuel cell with parallel gas distributors," *J Power Sources*, 195(9), pp. 2764-2773.
- [20] Parthasarathy, A., Srinivasan, S., Appleby, A. J., and Martin, C. R., 1992, "Pressure-Dependence of the Oxygen Reduction Reaction at the Platinum Microelectrode Nafion Interface - Electrode-Kinetics and Mass-Transport," *J Electrochem Soc*, 139(10), pp. 2856-2862.
- [21] Bernardi, D. M., and Verbrugge, M. W., 1992, "A Mathematical-Model of the Solid-Polymer-Electrolyte Fuel-Cell," *J Electrochem Soc*, 139(9), pp. 2477-2491.
- [22] Wu, H., Li, X., and Berg, P., 2009, "On the modeling of water transport in polymer electrolyte membrane fuel cells," *Electrochim Acta*, 54(27), pp. 6913-6927.

- [23] Springer, T. E., Zawodzinski, T. A., and Gottesfeld, S., 1991, "Polymer Electrolyte Fuel-Cell Model," *J Electrochem Soc*, 138(8), pp. 2334-2342.
- [24] Udell, K. S., 1985, "Heat-Transfer in Porous-Media Considering Phase-Change and Capillarity - the Heat Pipe Effect," *Int J Heat Mass Tran*, 28(2), pp. 485-495.
- [25] Ren, X. M., Price, S. C., Jackson, A. C., Pomerantz, N., and Beyer, F. L., 2014, "Highly Conductive Anion Exchange Membrane for High Power Density Fuel-Cell Performance," *Acs Appl Mater Inter*, 6(16), pp. 13330-13333.
- [26] Kruusenberg, I., Matisen, L., Shah, Q., Kannan, A. M., and Tammeveski, K., 2012, "Non-platinum cathode catalysts for alkaline membrane fuel cells," *Int J Hydrogen Energ*, 37(5), pp. 4406-4412.
- [27] Leng, Y. J., Wang, L. Z., Hickner, M. A., and Wang, C. Y., 2015, "Alkaline membrane fuel cells with in-situ cross-linked ionomers," *Electrochim Acta*, 152, pp. 93-100.
- [28] Rho, Y. W., Velez, O. A., Srinivasan, S., and Kho, Y. T., 1994, "Mass-Transport Phenomena in Proton-Exchange Membrane Fuel-Cells Using O₂/He, O₂/Ar, and O₂/N₂ Mixtures .1. Experimental-Analysis," *J Electrochem Soc*, 141(8), pp. 2084-2088.
- [29] Rho, Y. W., Srinivasan, S., and Kho, Y. T., 1994, "Mass-Transport Phenomena in Proton-Exchange Membrane Fuel-Cells Using O₂/He, O₂/Ar, and O₂/N₂ Mixtures .2. Theoretical-Analysis," *J Electrochem Soc*, 141(8), pp. 2089-2096.

TABLE CAPTIONS

Table 1 – Source term expressions

Table 2 – List of physical properties [10]

Table 3 – Electrochemical parameters

Table 4 – List of dimensions

Table 5 – Mesh independence – Effect of N^x , N^y and N^z on the error of the average current density and the non-dimensional minimum cell distance (i.e. $\emptyset = \Delta_{min,cell}/L$ where L is the largest dimension in the direction in question) and grid expansion ratio (r) values for the M5 mesh.

Table 6 – Source terms and domains

Table 7 – List of operating parameters [7]

Table 1 – Source term expressions

Source term	Unit
$S_{H_2} = -\frac{i_a}{2F} M_{H_2}$	$kg/(m^3s)$
$S_{O_2} = -\frac{i_c}{4F} M_{O_2}$	$kg/(m^3s)$
$S_{H_2O,rc} = -\frac{i_c}{2F} M_{H_2O}$	$kg/(m^3s)$
$S_{H_2O,ra} = \frac{i_a}{F} M_{H_2O}$	$kg/(m^3s)$
$S_{v-l} = \begin{cases} \gamma_{cond} \epsilon (1-s) \frac{M_{H_2O}}{RT} (p_{H_2O} - p_{sat}) & \text{if } p_{H_2O} \geq p_{sat} \\ \gamma_{evap} \epsilon s \frac{M_{H_2O}}{RT} (p_{H_2O} - p_{sat}) & \text{if } p_{H_2O} < p_{sat} \end{cases}$	$kg/(m^3s)$
$S_{mem} = \zeta_{mem} (\lambda_e - \lambda)$	$1/s$
$S_s = \begin{cases} i_a & \text{if } ACL \\ -i_c & \text{if } CCL \end{cases}$	A/m^3
$S_m = \begin{cases} -i_a & \text{if } ACL \\ i_c & \text{if } CCL \end{cases}$	A/m^3
$S_{E,ra} = i_a \left(\frac{T\Delta S}{2F} + \eta \right)$	W/m^3
$S_{E,rc} = i_c \eta $	W/m^3
$S_{E,ohm}^s = \ \nabla \phi_s\ ^2 \kappa_s^{eff}$	W/m^3
$S_{E,ohm}^m = \ \nabla \phi_m\ ^2 \kappa_m^{eff}$	W/m^3
$S_E^{eva/con} = h_{lat} S_{v-l}$	W/m^3
$S_E^{sor/des} = -h_{lat} \frac{\rho_{mem}}{EW} M_{H_2O} S_{mem}$	W/m^3

Table 2 – List of physical properties [10]

Parameter	Value	Unit
Thermal conductivity of CL, k_{CL}	1.0	(W/m·K)
Thermal conductivity of GDL, k_{GDL}	1.0	(W/m·K)
Thermal conductivity of membrane, k_{mem}	0.95	(W/m·K)
Thermal conductivity of BP, k_{BP}	20.0	(W/m·K)
Electrical conductivity in CL, $\kappa_{s,CL}$	750.0	S/m
Electrical conductivity in GDL, $\kappa_{s,GDL}$	750.0	S/m
Electrical conductivity in BP, $\kappa_{s,BP}$	20000.0	S/m
Specific heat of CL, $C_{p,CL}$	3300.0	(J/kg·K)
Specific heat of GDL, $C_{p,GDL}$	568.0	(J/kg·K)
Specific heat of membrane, $C_{p,mem}$	833.0	(J/kg·K)
Specific heat of BP, $C_{p,BP}$	1580.0	(J/kg·K)
Liquid water density, ρ_l	970.0	(kg/m ³)
Contact angle, θ	100	(°)
Dry density membrane, ρ_{mem}	1092.7	(kg/m ³)
Equivalent weight, EW	588.24	(kg/kmol)
Evaporation/Condensation rates, $\gamma_{evap,cond}$	100.0	(1/s)
Sorption/Desorption rates, ζ_{mem}	1.0	(1/s)
Entropy change of reaction in anode, ΔS	163303.5	(J/kmol·K)
Condensation latent heat, h_{lat}	2.395x10 ⁶	(J/kg)

Table 3 – Electrochemical parameters

Parameters	Anode	Cathode	Reference	Unit
Reference current density, j_0^{ref}	11.916	1×10^{-4}	[10],[28]	A/m_{Pt}^2
Hydrogen reference concentration, H_2^{ref}	0.0564	-	[10]	$kmol/m^3$
Oxygen reference concentration, O_2^{ref}	-	0.0021	[28]	$kmol/m^3$
Platinum loading, m_{Pt}	0.004	0.004	[11]	kg/m^2
Platinum mass ratio, %Pt	0.4	0.4	[11]	
Ionomer volume fraction, L_M	0.22	0.22	[10]	
Transfer coefficient, α	0.5	1.0	[29]	
Radius of agglomerate, r_{agg}	1×10^{-6}	1×10^{-6}	[11]	m
Thickness of ionomer covering each agglomerate, δ_{agg}	8×10^{-8}	8×10^{-8}	[11]	m

Table 4 – List of dimensions

Parameter	Value	Unit
Thickness of GDL, δ_{GDL}	2.0×10^{-4}	(m)
Thickness of CL, δ_{CL}	1.0×10^{-5}	(m)
Thickness of membrane, δ_{mem}	2.8×10^{-5}	(m)
Channel length, l	0.1	(m)
Channel width, w_c	5.0×10^{-4}	(m)
Channel height, h	1.0×10^{-3}	(m)
Rib width, w_r	5.0×10^{-4}	(m)
Intrinsic permeability of CL, K_{CL}^0	6.2×10^{-13}	(m ²)
Intrinsic permeability of GDL, K_{GDL}^0	6.2×10^{-12}	(m ²)
Porosities of GDL, ϵ_{GDL}	0.6	
Porosities of CL, ϵ_{CL}	0.3	

Table 5 – Mesh independence – Effect of N^x , N^y and N^z on the error of the average current density and the non-dimensional minimum cell distance (i.e. $\phi = \Delta_{min,cell}/L$ where L is the largest dimension in the direction in question) and grid expansion ratio (r) values for the M5 mesh.

	N^x	N^y	N^z		N^x	N^y	N^z		N^x	N^y	N^z
M1	8	10	100	M4	10	10	100	M7	10	10	80
M2	10			M5		15		M8			100
M3	12			M6		20		M9			120

	Err^x (%)		Err^y (%)		Err^z (%)
M1	2.12	M4	5.11	M7	3.21
M2	1.39	M5	2.14	M8	1.22
M3	1.24	M6	1.74	M9	0.97

	ϕ_x	ϕ_y	ϕ_z	r_x	r_y	r_z
Bipolar plate	0.1	2.643×10^{-5}	0.01	1	1.211	1
Flow channel		2.643×10^{-5}			1.211	
Gas diffusion layer		5.286×10^{-6}			1.211	
Catalyst layer		2.643×10^{-7}			1.211	
Membrane		7.400×10^{-7}			1.211	

Table 6 – Source terms and domains

Source term	ACL	CCL	Anode GDL	Cathode GDL	Membrane	BP
S_{mass}	$S_{H_2} + S_{H_2O}$	$S_{O_2} + S_{H_2O}$	S_{H_2O}	—	—	—
S_{H_2}	S_{H_2}	—	—	—	—	—
S_{O_2}	—	S_{O_2}	—	—	—	—
S_{H_2O}	$S_{H_2O,ra} - S_{v-l} + S_{mem} M_{H_2O} \frac{\rho_{mem}}{EW}$	$S_{H_2O,rc} + S_{mem} M_{H_2O} \frac{\rho_{mem}}{EW}$	$-S_{v-l}$	—	—	—
S_s	S_s	S_s	—	—	—	—
S_m	S_m	S_m	—	—	—	—
S_l	S_{v-l}	—	S_{v-l}	—	—	—
S_d	$-S_{mem}$	$-S_{mem}$	—	—	—	—
S_E	$S_{E,ra} + S_{E,ohm}^s + S_{E,ohm}^m + S_E^{eva/con} + S_E^{sor/des}$	$S_{E,rc} + S_{E,ohm}^s + S_{E,ohm}^m + S_E^{sor/des}$	$S_{E,ohm}^s + S_E^{eva/con}$	$S_{E,ohm}^s$	$S_{E,ohm}^m$	$S_{E,ohm}^s$

Table 7 – List of operating parameters [7]

Parameter	Value	Unit
Operating temperature, T_0	323.15	(K)
Relativity humidity at anode, RH_a	100	(%)
Relativity humidity at cathode, RH_c	100	(%)
Output voltage, V_{out}	0.3 - 1.0	(V)
Stoichiometry ratio at anode, ξ_a	2.0	
Stoichiometry ratio at cathode, ξ_c	3.0	

FIGURE CAPTIONS

Figure 1 – Schematic representation of PEM and AEM fuel cell. The product of both types of fuel cell is water, heat generation and electrical energy.

Figure 2 – a) Three-dimensional representation of the computational domain. b) Two-dimensional schematic representation of the computational domain and mesh.

Figure 3 - Catalyst layer composition scheme. The porous and Pt dispersed C are covered by an ionomer layer. As the species cross the ionomer layer covering the agglomerate, the reaction process takes place.

Figure 4 – Polarisation curve for both agglomerate and macro-homogeneous [10] catalyst layer numerical models along with experimental data [25-27].

Figure 5 – Total overpotential for both agglomerate and macro-homogeneous models.

Figure 6 - Concentration loss in the cathode catalyst layer: a) macro-homogeneous model b) agglomerate model

Figure 7 – Activation loss in the cathode catalyst layer: a) macro-homogeneous model b) agglomerate model.

Figure 8 – Effectiveness factor: a) anode catalyst layer b) cathode catalyst layer.

Figure 9 – Effect of temperature on the overall fuel cell performance. Solid line (—) macro-homogeneous model, dash line (- -) agglomerate model.

Figure 10 – Effect of relative humidity on the overall fuel cell performance. Solid line (—) macro-homogeneous model, dash line (- -) agglomerate model.

Figure 1 – Schematic representation of PEM and AEM fuel cell. The product of both types of fuel cell is water, heat generation and electrical energy.

Figure 2 – a) Three-dimensional representation of the computational domain. b) Two-dimensional schematic representation of the computational domain and mesh.

Figure 3 - Catalyst layer composition scheme. The porous and Pt dispersed C are covered by an ionomer layer. As the species cross the ionomer layer covering the agglomerate, the reaction process takes place.

Figure 4 – Polarisation curve for both agglomerate and macro-homogeneous [10] catalyst layer numerical models along with experimental data [25-27].

Figure 5 – Total overpotential for both agglomerate and macro-homogeneous models.

Figure 6 - Concentration loss in the cathode catalyst layer: a) macro-homogeneous model b) agglomerate model.

Figure 7 – Activation loss in the cathode catalyst layer: a) macro-homogeneous model b) agglomerate model.

Figure 8 – Effectiveness factor: a) anode catalyst layer b) cathode catalyst layer.

Figure 9 – Effect of temperature on the overall fuel cell performance. Solid line (—) macro-homogeneous model, dash line (- -) agglomerate model.

Figure 10 – Effect of relative humidity on the overall fuel cell performance. Solid line (—) macro-homogeneous model, dash line (- -) agglomerate model.