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A two dimensional agglomerate model for a proton exchange membrane fuel cell

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ABSTRACT

A two dimensional steady state and isothermal model of a proton exchange membrane fuel cell is presented. This model is applied to a fuel cell with a counter-flow mode of hydrogen and air along parallel flow channels. In the flow channel and porous media, reactant flow is modelled using the continuity and Navier–Stokes equation. Reactant diffusion and convection are modelled by the Maxwell–Stefan and Navier–Stokes equation, respectively. Water transport is described by the combined mechanism of electro-osmotic drag, back diffusion and hydraulic permeation. The catalyst layer is modelled as a spherical-agglomerate structure in which ionomer and liquid water partially occupy the void space to form a so-called carbon–ionomer–liquid water film inside the agglomerate. A mathematical relationship for the variation in film thickness with the current density is also developed. The effect of platinum and carbon loadings on the cell performance and effectiveness are simulated. The fuel cell polarisation curve based on the agglomerate with a film model gives good agreement to experimental data while the agglomerate without a film model overestimates the current density. The modelling results show that the rapid fall in current density at lower cell voltage is due to an increased oxygen diffusion resistance through the film.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising candidates for auto motive and small stationary applications due to their high electrical efficiency, power density and durability [1–3]. Although significant improvements with respect of cell performance, stability and cost have been achieved over the past decade, some barriers still hamper the commercial use of PEMFCs. The relatively poor oxygen reduction reaction (ORR) in the cathode catalyst layer (CCL) is one of the biggest obstacles holding back the PEMFC performance [4–11].

Numerous models have been developed to investigate the effect of the CCL on the PEMFC performance, for example, ultra-thin layer [4,8], pseudo-homogeneous [7,11] and agglomerate [6,9] models. The ultra-thin layer model is the simplest model requiring the least computational resource because the catalyst layer is assumed to behaviour as merely an interface between the gas diffusion layer (GDL) and the membrane. This model gives limited insight into the effect of composition on the performance of the catalyst layer. Due to the significant difference between the ultra-thin layer structure and the real three dimensional (3D) structure of the catalyst layer, the ultra-thin layer model typically overestimates the current density output of the PEMFC. An improved model developed by Marr and Li [7] was created based on the work of Bernardi and Verbrugge [5]. This model applied a pseudo-homogeneous thin layer as the cathode catalyst structure in which the CCL composition, such as platinum and ionomer loading, were investigated. This model indicated that good utilisation of the thin layer catalyst layer is difficult to achieve due to the greater ORR rate relative to the oxygen diffusion rate. However, this model, by assuming the void space of the catalyst layer is fully occupied by liquid water, failed to simulate the fuel cell performance accurately under a wild range of operating condition. Broka and Ekdunge [6] compared the pseudo-homogeneous film model with the agglomerate model and concluded that the latter gave a superior to represent the CCL than the pseudo-homogeneous film model. Sun et al. [9] developed an improved two dimensional (2D) cross the channel (CTC) spherical-agglomerate model for the cathode of the PEMFC. They showed that in this model both electron and proton transport were important in determining the local cathode overpotential and the electrochemical reaction rate, and that the oxygen transport resistance through the ionomer film surrounding the agglomerates was the main factor controlling the observed limiting current density.

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Nomenclature

A	cross-sectional area, m^2
a	specific area, m^{-1}
C	dimensionless concentration
c	concentration, mol m^{-3}
c_f	fixed charge concentration in membrane, mol m^{-3}
D_{ij}	Maxwell–Stefan diffusion coefficient matrix, m^2 s^{-1}
E^0	potential applied on the electrode, V
E_{cell}	cell voltage, V
E_r	effectiveness factor
F	Farady's constant, 96,485 C mol^{-1}
H	Henry's constant, Pa m^3 mol^{-1}
i	current density, A m^{-2}
i_0	exchange current density, A m^{-2}
k	reaction rate coefficient, s^{-1}
l	thickness, m
M_j	molecular weight for species j, kg mol^{-1}
M_n	mean molecular weight, kg mol^{-1}
m_{Pt}	platinum loading, mg cm^{-2}
m_C	carbon loading, mg cm^{-2}
N_j	molar flux of species j, mol m^{-2} s^{-1}
n_{drag}	electro-osmotic drag coefficient
n_{diff}	back diffusion coefficient
n_{hyd}	hydraulic permeation coefficient
p	pressure, Pa
Q	reactant gas flow rates, m^3 s^{-1}
R	ideal gas constant, 8.314 J mol^{-1} K^{-1}
R_M	membrane resistance, Ω m^{-2}
RH	relative humidity
r	radius, m
T	temperature, K
u	flow velocity, m s^{-1}
V	mole volume, m^3
w	mass fraction
x	mole fraction

Greek

α	charge transfer coefficient
α_{net}	net electro-osmotic drag coefficient
α_{H_2O}	water activity
κ_p	hydraulic permeability, m^2
λ	water content
μ	viscosity, Pa s
ρ	density, kg m^{-3}
ε	volume fraction
δ	film thickness, m
η	overpotential, V
σ	conductivity, Ω^{-1} m^{-1}
ξ	stoichiometric flow ratio
Φ_L	Thiele's modulus
ϕ	potential, V
ψ_{H_2O}	association parameter for water (the value is 2.6)

Superscripts

0	intrinsic
eff	effective
ref	reference
eq	equilibrium

Subscripts

a	anode
agg	agglomerate
C	carbon
c	cathode
CL	catalyst layer
GDL	gas diffusion layer
I	ionomer
i	species i
j	species j
M	membrane
Pt	platinum
Pt/C	platinum dispersed carbon
s	solid phase (electrode)
W	water

However, presence of the liquid water was not considered in this model.

Water management is an important issue in PEMFCs that use perfluorinated membrane such as Nafion®. The earliest water management models were developed by Springer et al. [4], Bernardi and Vebrugge [5], and Nguyen and White [12]. The first one dimension (1D) steady state model, developed by Springer et al. [4], described water diffusion coefficients, electro-osmotic drag coefficients and membrane conductivity as function of water content in the Nafion® 117 membrane. The model developed by Bernardi and Vebrugge [5] used a porous electrode instead of the ultrathin film electrode which was applied by Springer et al. [4]. Water transport through the membrane was associated with hydraulic pressure and the potential gradients. This model gave comprehensive profiles of concentration, pressures and water velocity through the membrane electrode assembly (MEA) including the anode catalyst layer (ACL), membrane and CCL. Heat management was combined with water management in the model developed by Nguyen and White [12]. The model focused on the effect of inlet gas humidity on the cell performance in which water migration and back diffusion accounted for the net water flux through the membrane. However, the effect of hydraulic permeation through membrane was not included. Ge and Yi [13] developed a 2D steady state model to describe water transport through the membrane with fuel and oxidant gases in co-flow and counter-flow modes. In this model, three water transport mechanisms; electro-osmotic drag, back diffusion and hydraulic permeation were all considered. This so-called combinational model was successfully applied in previous work [14–18]. In recent years, computational fluid dynamic (CFD) model combined with volume of fluid (VOF) and multi-phase mixture (M^2) method were developed for water droplet formation, accumulation and then two phase flow within the GDL [19–22].

Although the previous models of the PEMFC have given several important insights for optimisation of the CCL composition and operating conditions, other additional aspects of the PEMFC should be included to try to improve the simulation of the fuel cell operated under various practical conditions. One of these is to consider the hydrogen oxidation reaction (HOR) at anode into the model simultaneously when simulating the cathode. A second aspect is to develop a relationship between the liquid water film thickness and the current density and fuel cell operating condition, such as temperature and pressure. The aim of this work is to develop a 2D along the channel (ATC) model based on a spherical-agglomerate catalyst structure combined with the water transport mechanism, to investigate the effect of catalyst layer parameters and operating conditions on the liquid water film thickness and the effectiveness factor of the catalyst layer and the performance of the cell. This model can give useful guidance for optimisation of the catalyst layer composition.

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