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Generalized flooded agglomerate model for the cathode catalyst layer of a polymer electrolyte membrane fuel cell

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ABSTRACT

The flooded agglomerate model has found prolific usage in modeling the oxygen reduction reaction within the cathode catalyst layer of a polymer electrolyte membrane fuel cell (PEMFC). The assumption made in this model is that the ionomer-coated carbon–platinum agglomerate is spherical in shape and that the spheres are non-overlapping. This assumption is convenient because the governing equations lend themselves to closed-form analytical solution when a spherical shape is assumed. In reality, micrographs of the catalyst layer show that the agglomerates are best represented by sets of overlapping spheres of unequal radii. In this article, the flooded agglomerate is generalized by considering overlapping spheres of unequal radii. As a first cut, only two overlapping spheres are considered. The governing reaction-diffusion equations are solved numerically using the unstructured finite-volume method. The volumetric current density is extracted for various parametric variations, and tabulated. This sub-grid-scale generalized flooded agglomerate model is first validated and finally coupled to a computational fluid dynamics (CFD) code for predicting the performance of the PEMFC. Results show that when the agglomerates are small (<200 nm equivalent radius), the effect of agglomerate shape on the overall PEMFC performance is insignificant. For large agglomerates, on the other hand, the effect of agglomerate shape was found to be critical, especially for high current densities for which the mass transport resistance within the agglomerate is strongly dependent on the shape of the agglomerate, and was found to correlate well with the surface-to-volume ratio of the agglomerate.

1. Introduction

One of the major impediments to commercial success of hydrogen–oxygen fuel cells is the cost associated with the excessive use of platinum within the catalyst layers. In a polymer electrolyte membrane fuel cell (PEMFC), since the catalyst (platinum) is dispersed within a complex porous matrix comprised of carbon, the ionomer (Nafion) and platinum, the performance of the fuel cell has a convoluted relationship with an increase in the amount of platinum within the catalyst layer. Rather than the amount of platinum, the performance depends on how the platinum is dispersed within the porous matrix so that it is effectively utilized in catalyzing the electrochemical reactions. Thus, there is strong motivation for optimization of the catalyst layers of a PEMFC. Since the proper functioning of a PEMFC cathode requires existence of triple phase boundaries [1,2] between the ionomer (for proton transfer), platinum (for catalysis) and carbon (for electron transfer), the determination of optimum composition and structure of the catalyst layer is a monumental task. Such studies are often undertaken using experiments [3,4], but are very time-consuming and expensive. Computational modeling provides an alternative pathway to address this critical issue.

Model-based optimization of the cathode catalyst layer of a PEMFC has been a topic of intense research over the past two decades. Models used for this purpose may be broadly categorized as: (1) models that utilize the pseudo-homogeneous film concept [5–9], or the flooded agglomerate concept [10–28], and (2) direct numerical simulation (DNS) of the catalyst layer [29–33]. While the latter approach is more first-principles and general, it is usually performed at a much smaller scale and is cumbersome for coupling to a device-scale model. First, it requires reconstruction of the catalyst layer microstructure from micrographs. Secondly, direct numerical solution of the transport-reaction equations within the complex catalyst layer structure are difficult to perform and are very expensive. Simulation times for a single case may often run into days. This makes this approach impractical for engineering calculations. Nevertheless, direct numerical simulations are very useful for fundamental understanding of the coupling between transport and reactions at the pore scale of the cathode catalyst layer.

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Nomenclature

A_f	area of face f of control volume (m^2)
A_v	total catalyst surface area per unit volume of anode or cathode (m^{-1})
c	dissolved oxygen concentration in Nafion (kmol m^{-3})
c^*	dissolved oxygen concentration in Nafion in equilibrium with inlet gas (kmol m^{-3})
c_0^{ref}	standard reference oxygen concentration (kmol m^{-3})
$c_{O_2,g}$	oxygen gas concentration in cathode gas pores (kmol m^{-3})
$c^*_{O_2,g}$	oxygen gas concentration at cathode inlet (kmol m^{-3})
$\bar{d}$	average pore size of cathode (m)
$\mathcal{D}_{kn}$	binary diffusion coefficient of species k into n ($m^2\,s^{-1}$)
D_λ	diffusion coefficient of water ($m^2\,s^{-1}$)
D'_λ	concentration dependence of D_λ, dimensionless
D_T	temperature dependence of D_λ, ($m^2\,s^{-1}$)
$D_{O_2,N}$	diffusion coefficient of oxygen in Nafion ($m^2\,s^{-1}$)
$D_{O_2,N}^{eff}$	effective diffusion coefficient of oxygen in Nafion in agglomerate ($m^2\,s^{-1}$)
F	Faraday's constant (96.487×10^6 C $kmol^{-1}$)
$\mathbf{i}$	net current density vector (A m^{-2})
$\mathbf{i}_F$	ionic phase current density vector (A m^{-2})
i_0^{ref}	standard exchange current density on cathode (A m^{-3})
$\mathbf{i}_S$	electronic phase current density vector (A m^{-2})
i_s^{cat}	surface current density on catalyst surface of cathode (A m^{-2})
$\mathbf{J}_k$	diffusion mass flux of the kth species (kg $m^{-2}\,s^{-1}$)
j_T^{an}	net transfer current at anode (A m^{-3})
j_T^{cat}	net transfer current density at cathode (A m^{-3})
j_0	reference current density (A m^{-2})
L	cathode catalyst layer thickness (m)
m_{Pt}	platinum mass loading (kg m^{-2})
M_m	molar mass of the membrane (kg $kmol^{-1}$)
M_k	molecular weight of kth species (kg $kmol^{-1}$)
n	number of electrons transferred during the electrochemical reaction
$\widehat{n}$	number of agglomerates per unit volume of cathode (m^{-3})
$\hat{\mathbf{n}}_f$	unit surface normal at control volume face
N	total number of gas-phase species
p	pressure (Pa)
Pt|C	platinum–carbon mass ratio in catalyst layer ink, dimensionless
r_{agg}	radius (actual or equivalent) of agglomerate (m)
r_1, r_2	radii of the two overlapping spheres (m)
R	universal gas constant (8314 J $kmol^{-1}\,K^{-1}$)
$\dot{S}_k$	production rate of kth species (kg $m^{-3}\,s^{-1}$)
T	absolute temperature (K)
U	bulk fluid velocity (m s^{-1})
V_{agg}	total volume of agglomerate (m^3)
V_{nuc}	volume of nucleus of agglomerate (m^3)
V_{ctg}	volume of coating (m^3)
V_O	volume of cell or control volume O (m^3)
Y_k	mass fraction of kth species
Greek	
α_a, α_c	Tafel constants for anode, dimensionless
α_T	Tafel constant for cathode catalyst model, dimensionless
β_k	concentration exponents for the kth species
δ	polymer coating thickness around agglomerate nucleus (m)
ε	wet porosity, dimensionless
ε_{agg}	volume fraction of polymer in agglomerate nucleus, dimensionless
ε_{cat}	porosity of cathode catalyst layer, dimensionless
ε_S	volume fraction of platinum + carbon in cathode, dimensionless
ε_N	volume fraction of polymer in cathode, dimensionless
η	electrode overpotential (V)
η_d	electro-osmotic drag coefficient, dimensionless
κ	permeability (m^2)
λ	water content, dimensionless
$[\Lambda_k]$	molar concentration of species k (kmol m^{-3})
μ	dynamic viscosity (kg $m^{-1}\,s^{-1}$)
ρ	mass density of mixture (kg m^{-3})
ρ_m^{dry}	density of dry membrane (kg m^{-3})
σ	electrical conductivity ($\Omega^{-1}\,m^{-1}$)
σ_F	electrical conductivity of the ionic phase ($\Omega^{-1}\,m^{-1}$)
σ_S	electrical conductivity of the electronic phase ($\Omega^{-1}\,m^{-1}$)
σ_{30}	concentration dependence of electrical conductivity ($\Omega^{-1}\,m^{-1}$)
ϕ_F	ionic phase potential (V)
ϕ_S	electronic phase potential (V)
ϕ_{OC}	open circuit voltage (V)
τ_{cat}	tortuosity of cathode, dimensionless
ξ	overlap parameter, dimensionless

The more popular approach is based on hypothesized models of coupled mass transport and reactions within the catalyst layer structure. Historically, two different model types have been used for this purpose. The first model type, generally referred to in the literature as the pseudo-homogeneous film model [5–9], assumes that the catalyst layer is a porous matrix comprised of Nafion, platinum, and carbon in random (homogeneous) configuration. This model allows for pathways of gases, electrons, and protons within the catalyst layer, and captures some of the essential transport phenomena prevalent in the catalyst layer. However, this model does not acknowledge the necessity for the existence of the triple-phase boundary for a functioning catalyst layer. In contrast, the flooded agglomerate concept, proposed in the late 1980s [10,11], contends that the platinum is supported on carbon particles, which forms agglomerates when mixed with an ionomer. The agglomerate may even be coated fully or partially by an additional ionomer layer. The oxygen finds its way to the platinum by first dissolving in the ionomer, and is consumed as it transports to the core of the carbon–platinum aggregate. This model guarantees the existence of triple-phase boundaries as long as sufficient amounts of the ionomer are present. Calculations performed using this model appear to match experimental data better than the pseudo-homogeneous film model [8,19]. Most notable among early studies that have used the flooded agglomerate model is the work of Jaouen et al. [15,16,34], Sun et al. [18], and Secanell et al. [19], although this model has found prolific usage more recently. Jaouen et al. have successfully used this model to predict the performance of the cathode as a function of operating conditions and cathode layer thicknesses. Their calculations predicted experimentally observed double Tafel slopes [16], attributed to local (within agglomerate) mass