



## Method to improve catalyst layer model for modelling proton exchange membrane fuel cell



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### HIGHLIGHTS

- We prove how to derive a model to calculate average oxygen reduction rate.
- We show how to calculate the model parameters for a given catalyst layer structure.
- We validate the model against experimental data.
- We investigate the relative significance of different resistances to oxygen reduction.

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### ABSTRACT

Correctly describing oxygen reduction within the cathode catalyst layer (CL) in modelling proton exchange membrane fuel cell is an important issue remaining unresolved. In this paper we show how to derive an agglomerate model for calculating oxygen reactions by describing dissolved oxygen in the agglomerates using two independent random processes. The first one is the probability that an oxygen molecule, which dissolves in the ionomer film on the agglomerate surface, moves into and then remains in the agglomerates; the second one is the probability of the molecule being consumed in reactions. The first probability depends on CL structure and can be directly calculated; the second one is derived by assuming that the oxygen reduction is first-order kinetic. It is found that the distribution functions of the first process can be fitted to a generalised gamma distribution function, which enables us to derive an analytical agglomerate model. We also extend the model to include oxygen dissolution in the ionomer film, and apply it to simulate cathode electrodes. The results reveal that the resistance to oxygen diffusion in ionomer film and agglomerate in modern CL is minor, and that the main potential loss is due to oxygen dissolution in the ionomer film.

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### 1. Introduction

Species transport and electrochemical reactions in the gas-diffusion layer (GDL) and catalyst layer (CL) within the polymer electrolyte membrane (PEM) fuel cell occur at pore scale. In practical fuel cell modelling, however, the geometries of these pores cannot be explicitly resolved, and their impact on different fuel cell

processes is instead described by volumetric average parameters, such as effective diffusion coefficients for species diffusion and effective conductivities for charge transport [1]. How to accurately describe these pore-scale processes in a fuel cell model is crucial, and the most challenging one is the description of oxygen diffusion and reaction in the cathode CL [2,3].

Most catalyst layers in PEM fuel cells use carbon grains to support the catalyst, and the carbon grains are further bound by an ionomer [4,5]. During manufacturing, the carbon grains tend to aggregate, forming porous agglomerates [6] with their outer surfaces coated by a thin ionomer film [7,8]. As such, the catalyst layer has a bi-mode pore structure in which the pores inside the agglomerates (intra-agglomerate pores) are much smaller than the

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Nomenclature			
$A_l$	Specific outer surface area of ionomer film	$k_d^o$	Gaseous oxygen dissolution rate coefficient in ionomer film
$c'$	Concentration of dissolved oxygen within agglomerates	$N_i$	Molar flux of gas $i$ in inter-agglomerate pores
$C_i$	Average molar concentration of gas $i$ in inter-agglomerate pores	$p_o$	Partial pressure of gaseous oxygen in inter-agglomerate pores
$C_o$	Concentration of dissolved oxygen in outer surface of ionomer film	$R$	Gas constant
$C$	Total molar concentration of all gases in inter-agglomerate pores	$R_m$	Resistance of the membrane
$C^{eq}$	Concentration of dissolved oxygen in equilibrium with gaseous oxygen in inter-agglomerate pores	$R_0(t)$	Mass of dissolved oxygen in agglomerate at time $t$
$C_{ref}$	Reference dissolved oxygen concentration	$R_e(t)$	Average oxygen reduction rate in the catalyst layer at time $t$
$D_o$	Diffusion coefficient of dissolved oxygen in ionomer	$S_a$	Volumetric reactive surface area of catalyst in agglomerate
$D'$	Effective diffusion coefficient of dissolved oxygen in agglomerates	$T$	Temperature
$D_{ij}^{eq}$	Effective binary diffusion coefficient of gases $i$ and $j$ in CL and GDL	$V_i$	Volume of voxel in the 3D image of the reconstructed catalyst layer
$D_{ij}$	Binary diffusion coefficient of gases $i$ and $j$ in free space	$v_i$	Average volume of the ionomer in each agglomerate voxel
$E_f^*$	Effectiveness factor of agglomerate model	$\alpha_c$	Cathode transfer coefficient
$E_{th}$	Theoretical oxygen reduction potential	$\beta$	Agglomerate model parameter
$E$	Cell voltage	$\alpha$	Agglomerate model parameter
$f_{in}(\varphi)$	Tortuosity of GDL in in-plane direction	$k$	Agglomerate model parameter
$f_{thru}(\varphi)$	Tortuosity of GDL in through-plane direction	$\eta$	Local overpotential
$F$	Faraday constant	$\varphi$	GDL porosity
$H_{O_2}$	Henry's constant for oxygen dissolution in ionomer	$\phi_s$	Solid potential
$I$	Average current density	$\phi_m$	Electrolyte potential
$i$	Local current density	$\sigma_m$	Protonic conductivity of CL
$i_{ref}$	Reference exchange current density	$\sigma_s$	Electronic conductivity of GDL and CL
$k_c$	Average oxygen reduction rate coefficient in agglomerate	$\theta$	Intra-agglomerate porosity
		$\varepsilon$	Size of the voxels in the 3D CL images
		$\lambda$	Average thickness of the ionomer film

pores between the agglomerates (inter-agglomerate pores). The ionomer film provides pathway for protons to transport, whilst the inter-agglomerate pores provide pathways for gaseous species to move [9].

In the cathode CL, gaseous oxygen moves from the GDL into the inter-agglomerate pores first, and then dissolves in the liquids before moving into the catalyst sites within the agglomerate to electrochemically react with protons and electrons [10]. In fuel cell modelling, the movement of gaseous oxygen in the inter-agglomerate pores is often assumed to be diffusive and modelled by a volumetric average diffusion equation. The diffusion and reaction of the dissolved oxygen within the agglomerate, however, cannot be explicitly resolved. Instead, they are treated as a sink term and calculated by a method known as agglomerate model in the literature [11].

The oxygen needs to overcome a number of resistances, including its dissolution in the ionomer film and the consequent diffusion in the ionomer film and the agglomerate [12], before it can react with electron and proton on the catalyst sites. The relative significance of each resistance, however, is poorly understood. With a few exceptions [13–15], the most common method used in the literature to describe these resistances is the spherical agglomerate model by idealising the CL as a packing of isolated spheres [16,17]. This idealisation not only oversimplifies the CL structure [4,18–21], but is also self-defeating. For example, its assumption of isolated and non-touched spheres physically makes the CL insulate to electrons as electrons can only transport through the carbon grains. Hence, the spherical agglomerate model is just to introduce a resistance to oxygen diffusion rather than a geometrical description of the CL structure. This explains why the agglomerate diameter

used in the spherical agglomerate model varies so widely in the literature, ranging from 200 nm to 6000 nm, far bigger than the average agglomerate size revealed by tomography, which is approximately 100 nm [22,23]. The thickness of the ionomer film used in the spherical models is up to 80 nm, also much thicker than real ionomer film, which is only about 10 nm thick [5]. The inferiority of the spherical model is well known, but still remains the dominant models in the literature due to the lack of alternatives [3,24–28].

There has been an increase over the past few years in use of nano-tomography to characterise CL at resolutions of a few nanometres [4,18–20,29]. This makes simulation of oxygen diffusion and reduction in a real CL feasible, and can be used to directly calculate the electrochemical reaction rate without need to simplify the CL structure [30,31]. The concern over this direct method is its computational cost. In fuel cell modelling, the CL is often divided into a number of grids. Since the reaction rate depends on overpotential, which varies spatially in the CL, the above direct method needs to calculate the reaction rate in each numerical grid using pore-scale simulation; this is computationally expensive. For practical use, therefore, it is ideal to derive a simple formula that can adequately describe the average reaction rate by explicitly taking all agglomerate processes into account. We made such an effort by assuming that the ionomer film was thin [32]. In this paper, we show how to derive the agglomerate model for a given agglomerate structure by describing oxygen movement and reaction within it as two independent random processes. We also apply the model to simulate a cathode electrode in an attempt to elucidate the relative significance of each resistance to oxygen diffusion in the agglomerates.

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