



# A proposed agglomerate model for oxygen reduction in the catalyst layer of proton exchange membrane fuel cells



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## ABSTRACT

Oxygen diffusion and reduction in the catalyst layer of PEM fuel cell is an important process in fuel cell modelling, but models able to link the reduction rate to catalyst-layer structure are lack; this paper makes such an effort. We first link the average reduction rate over the agglomerate within a catalyst layer to a probability that an oxygen molecule, which is initially on the agglomerate surface, will enter and remain in the agglomerate at any time in the absence of any electrochemical reaction. We then propose a method to directly calculate distribution function of this probability and apply it to two catalyst layers with contrasting structures. A formula is proposed to describe these calculated distribution functions, from which the agglomerate model is derived. The model has two parameters and both can be independently calculated from catalyst layer structures. We verify the model by first showing that it is an improvement and able to reproduce what the spherical model describes, and then testing it against the average oxygen reductions directly calculated from pore-scale simulations of oxygen diffusion and reaction in the two catalyst layers. The proposed model is simple, but significant as it links the average oxygen reduction to catalyst layer structures, and its two parameters can be directly calculated rather than by calibration.

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## 1. Introduction

Platinum supported by carbon grains is often used as the catalyst in proton exchange membrane (PEM) fuel cell [1]. The carbon grains are further bound by an ionomer to make the catalyst layer [2]. In manufacturing, the grain particles tend to aggregate, forming agglomerates with the nanopores (intra-agglomerate pores) inside them much smaller than the pores (inter-agglomerate pores) between them. In the cathode, gaseous oxygen moves into the inter-agglomerate pores first from the gas diffusion layer, and then diffuses into the agglomerates where it reacts with proton and electron, in the presence of the catalyst, to form water [3]. The catalyst layer has a bi-mode pore structure, but these pores cannot be explicitly resolved in fuel cell modelling. Instead, their impacts on oxygen diffusion and reaction are described by volumetric average parameters: effective diffusion coefficient for

gaseous oxygen diffusion in the inter-agglomerate pores and agglomerate model for oxygen diffusion and reaction inside the agglomerates [4,5].

The agglomerates in catalyst layers are geometrically complicated [6,7]. In earlier fuel cell modelling, oxygen diffusion through the pores inside the agglomerates was assumed to be fast and the potential loss due to it was often neglected [8]. This assumption is only rationale at low overpotential, in which the electrochemical reaction rate is slow and oxygen diffusion through the agglomerates is comparably fast. As a result, oxygen distribution within the agglomerates is relatively uniform and its accessibility to all catalyst particles inside the agglomerates is almost the same. When a cell works at high overpotential, however, the electrochemical rate is comparable to the maximum oxygen diffusion rate. This would create a concentration gradient, in which the catalysts in the proximity of the agglomerate surfaces have a better accessibility to oxygen than the catalysts in other areas. Therefore, the efficiency of the catalysts reduces, and oxygen diffusion becomes a limiting factor [9]. How to describe the impact of such oxygen-diffusion limitations on electrochemical reaction is essential to help catalyst layer design, and has attracted increased attention over the past few years [10,11].

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**Nomenclature**

$c$	concentration of dissolved oxygen within agglomerates
$c_{im}$	volumetric average of $c$ over the agglomerates
$c_m$	average dissolved oxygen concentration on the inner surface of agglomerates
$C$	gaseous oxygen concentration in the inter-agglomerate pores
$C_{eq}$	dissolved oxygen concentration in ionomer in equilibrium with $C$
$C_{ref}$	reference dissolved oxygen concentration
$D$	effective diffusion coefficient of the inter-agglomerate pores for gaseous oxygen
$D_0$	diffusion coefficient of ionomer for dissolved oxygen
$D_{eff}$	effective diffusion coefficient of intra-agglomerate pores for dissolved oxygen
$E$	effectiveness factor in the absence of ionomer film
$E'$	effectiveness factor in the presence of ionomer film
$F$	Faraday constant
$i_{ref}$	reference exchange current density
$k_c$	oxygen reduction rate
$M(t)$	mass of dissolved oxygen in agglomerates at time $t$
$r_{gg}$	radius of spherical agglomerates
$r(t)$	increasing rate of dissolved oxygen in agglomerates at time $t$
$R$	gas constant
$R_0$	consumption rate of gaseous oxygen in inter-agglomerate pores
$R_e$	average oxygen reduction rate in the agglomerates
$S_a$	volumetric reactive surface area of the catalyst in agglomerates
$S_0$	specific outer surface area of agglomerates
$T$	temperature
$V_i$	volume of each voxel in the 3D image of the catalyst layer
$v_i$	average volume of ionomer in each agglomerate voxel
$\alpha$	mass exchange rate coefficient between oxygen in intra-agglomerate and inter-agglomerate pores
$\alpha_c$	cathodic transfer coefficient
$\beta$	equilibrium constant between gaseous oxygen and oxygen dissolved in ionomer
$\eta$	overpotential
$\theta_{im}$	volumetric ionomer content in the intra-agglomerate pores
$\theta_m$	inter-agglomerate porosity
$\alpha$	agglomerate model parameter
$\kappa$	agglomerate model parameter
$\varepsilon$	size of voxel in the 3D images
$\lambda$	thickness of the ionomer film

The models that aim to describe the decrease in electrochemical reaction due to oxygen-diffusion limitations are known as agglomerate model in the literature. Apparently, the only available agglomerate model is the so-called spherical agglomerate model [12]. The assumption of the spherical model is that the agglomerates in the catalyst layer are non-touched spheres with the same diameter. Real agglomerates, however, are more geometrically complicated and approximating them by a number of non-touched spheres with a single diameter is an obvious oversimplification [13,14]. Since oxygen reaction in the catalyst layer depends on oxygen diffusion from the inter-agglomerate pores into the intra-agglomerate pores, which in turn depends on

the agglomerate geometry, the spherical model is inadequate to describe oxygen reduction when oxygen diffusion becomes a limiting factor. In fact, recent work has shown that when approximating the oxygen reaction in a given catalyst layer using the spherical model, its agglomerate diameter is just a fitting parameter rather than a geometrical description of the agglomerates; the value of its agglomerate diameter needs to change with overpotential in order to correctly describe the average reaction rate [15,16].

The average oxygen reaction in a catalyst layer depends on its geometry and oxygen diffusion in its agglomerates. Because the oxygen diffusion and reaction are difficult to measure, pore-scale modelling and tomography have been used increasingly in the past few years to bridge this gap [17,18]. For example, using X-ray tomography or focused ion beam/scanning electron microscopy (FIB/SEM) tomography, one can visualise the interior structures of a catalyst layer at resolutions as fine as a few nanometres [7,19]. These, together with the development in computational physics, have substantially improved our understanding of some fundamental transport and reaction processes in the catalyst layer, which would remain unknown otherwise [20–22]. There has been a surge in use of tomography and pore-scale model over the past few years to visualise and simulate catalyst layers [23]. For a catalyst layer with its 3D structure acquired by tomography, one can numerically calculate the average oxygen reduction rate within it under different operating conditions and then save the results in tabular forms as an input database for fuel cell modelling [15]. This database, however, could become extremely huge and time-consuming to obtain if a variety of operating conditions need to be considered. Therefore, it is practically useful if we can find a simple formula to represent this database.

The purpose of this paper is to present such a formula. To derive the formula, we first establish the link between the average oxygen reaction rate and a probability that an oxygen molecule, which is initially on the agglomerate surfaces, enters and then remains in the agglomerates at any time in the absence of any electrochemical reactions. We explain how to directly calculate the distribution function of this probability based on pore-scale simulation of oxygen diffusion, and then apply it to two catalyst layers with contrasting structures. The first one is an idealised catalyst layer packed by non-overlapped spheres, and the second one is a real catalyst layer acquired using FIB/SEM tomography. A formula is proposed to describe the distribution function of this probability calculated from the two samples, from which an agglomerate model is analytically derived. We verify the model by first showing that it is an improvement and can produce all the spherical agglomerate model can describe, and then testing it against the average electrochemical reaction rates directly calculated from pore-scale simulations of oxygen diffusion and reaction in the two catalyst layers under different overpotentials

**2. Background and theory**

Practical fuel cell modelling focuses on large scale and cannot explicitly resolve the individual pores within the catalyst layer where the electrochemical reaction takes place. In these models, all processes occurring at the pore scales are volumetrically averaged. In averaging the catalyst layer, the impact of the inter-agglomerate pores is represented by an effective diffusion coefficient, and the impact of the intra-agglomerate pores and catalyst loading are described by an agglomerate model [10,24]. In macroscopic fuel cell modelling, the combination of gaseous oxygen diffusion in the inter-agglomerate pores and oxygen diffusion and reduction in the intra-agglomerate pores are described by

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