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Modelling the mode of operation of PEMFC electrodes at the particle level: influence of ohmic drop within the active layer on electrode performance*

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Numerical modelling of charge transfer using the finite element method within the whole active layer of proton exchange membrane fuel cell (PEMFC) electrodes is proposed in order to study the electrocatalyst utilization as characterized by the effectiveness factor. In this way, two modified approaches based on the thin film and agglomerate models are developed for studying ionic ohmic drop effects in the active layer at both the electrolyte layer and electrocatalyst particles scales. The catalyst phase is considered to be a network of spherical nanoparticles instead of the classical representation as a uniform distribution over a surface (thin film model) or in a volume (agglomerate model). Simulations point out unexpected effects at the local level due to the discrete distribution of the catalyst phase as nanoparticles. Finally, the results are applied to the practical case of oxygen reduction and hydrogen oxidation.

Keywords: *P.E.M. fuel cells*, *active layer*, *particle level*, *charge transfer*, *modelling*

List of symbols

a	interparticle distance (m)
b	Tafel slope ($\mathrm{V\,dec^{-1}}$)
d	mean particle diameter (m)
F	Faraday constant ($96\,500\ \mathrm{C\,mol^{-1}}$)
l	Nafion layer thickness (m)
i	current density ($\mathrm{A\,m^{-2}}$)
i_o	exchange current density per real catalyst area ($\mathrm{A\,m^{-2}}$)
L	active layer thickness (m)
n	total number of electrons involved in the electrochemical reaction
R	gas constant ($8.31\ \mathrm{J\,K^{-1}\,mol^{-1}}$)
T	temperature (K)

Greek symbols

α	transfer coefficient
ε	effectiveness factor
Φ	potential (V)
γ	real catalyst area / geometric area ratio
η	local overpotential (V)
κ	ionic conductivity within the electrolyte phase ($\mathrm{S\,m^{-1}}$)

Index

i	index referring to the electrolyte membrane–particle interface
o	index referring to the gas–electrolyte interface

1. Introduction

Efficient proton exchange membrane fuel cells (PEMFC) require electrical characteristics such as high current density and voltage as well as a minimum volume. They also require minimum catalyst loading (platinum) without lowering performance. Modelling mass and charge transfer appears to be indispensable to predict and optimize the PEMFC electrode characteristics.

Many macroscopic models, such as the flooded agglomerate and thin film models, have been developed to describe the working behaviour of these electrodes. All these models consider the active layer to be a continuous medium of carbon-supported catalyst and recast Nafion®. Consequently they are not able to identify possible effects resulting from the discrete distribution of the catalyst phase in the shape of spherical nanoparticles. Stonehart [1] has suggested that an interparticle effect occurs at the local level due to the mutual influence of particles on diffusion when they are close together. Therefore it is important to check if present attempts to increase the Pt/C ratio offer a realistic way of improving PEMFC electrodes or risk failure because of limitations at the particle level .

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In previous work [2, 3], we investigated mass transfer limitations from the whole active layer level to the particle level. We showed the theoretical influence of some geometrical effects at the local level on transfer when considering diffusion and electrochemical reaction without ohmic drop. The present work offers a microscopic approach, studying ohmic drop and electrochemical reaction without diffusion limitation, within the active layer. This provides information on the competition effect between neighbouring particles and the ionic ohmic drop limitation, not only for the whole active layer, but also at the particle level. The results of the models are discussed with reference to the hydrogen/oxygen PEM fuel cell in order to optimize both the geometry of the active layer and the distribution of catalytic nanoparticles at, or close to, the gas–electrolyte interface.

2. Classical models

The porous active layer of a PEMFC electrode consists of a solid polymer electrolyte (Nafion®) providing good ionic conduction and an electrocatalyst (platinum) deposited on carbon grains. Platinum is a good catalyst for oxygen reduction and hydrogen oxidation reactions in an acidic medium and many studies have been performed to determine its properties under such conditions [4, 5]. Two main types of model have been proposed to describe the mode of operation of PEFMC electrodes: the homogeneous flooded model [6] and thin film models [7, 8]. These can be used to deduce the current-voltage curves of such electrodes by considering the active layer as a continuous medium of carbon-supported catalyst and recast Nafion®. They generally use a Tafel law to describe charge transfer kinetics at the catalyst surface.

This last assumption results from the Butler–Volmer law:

$$i = i_o\left[\frac{C_{ox}}{C_{ox}^{o}}\exp\left(\frac{\alpha nF\,\eta}{RT}\right) - \frac{C_{red}}{C_{red}^{o}}\exp\left(\frac{-(1-\alpha)nF\,\eta}{RT}\right)\right] \tag{1}$$

which can be reduced, in the absence of any concentration gradient, to a single cathodic or anodic term far from equilibrium, that is, for medium or high values of current density.

For a PEMFC, the reduction reaction is characterized only by a cathodic term:

$$-i = i_o\left[\exp\left(\frac{-(1-\alpha)nF|\eta|}{RT}\right)\right] \tag{2a}$$

and the oxidation reaction by an anodic term (2b):

$$i = i_o\left[\exp\left(\frac{\alpha nF\,\eta}{RT}\right)\right] \tag{2b}$$

Kinetics can therefore be characterized by a single equation using the slope b of the Tafel line: $b = 2.3\,RT/\alpha nF$ or $2.3\,RT/(1-\alpha)\,nF$.

The reactant diffuses into the Nafion® phase and simultaneously reacts [9] at the catalyst interface. For an isothermal system under steady state conditions without any concentration gradient, the one dimensional master equation can be written as:

$$\frac{\partial^2 Y}{\partial x^2} - V\exp(Y) = 0 \tag{3}$$

This equation describes potential or overpotential distribution in the catalyst layer from the dimensionless parameters Y and V defined as

$$Y = \frac{2.3|\eta|}{b} \quad \text{and} \quad V = 2.3\,\gamma i_0 L/\kappa b \tag{4}$$

based on the overpotential η, the exchange current density i_0 and the slope b of the Tafel line.

The model, therefore, solves Equation 3 using a numerical Runge–Kutta method taking into account the boundary conditions: (i) an overpotential at the membrane-active layer interface and (ii) zero ionic current density at the gas-active layer interface.

The flooded model considers that the Nafion® and the carbon supporting the electrocatalyst phase are evenly distributed throughout the volume [9]. As a consequence this model cannot take into account the presence of gas pores within the catalyst layer and therefore implies very strong diffusion limitations.

The thin film model assumes that the catalyst is distributed over a smooth surface under a thin film of electrolyte [10]. It considers gas pores and therefore the ohmic drop limitations are no longer negligible.

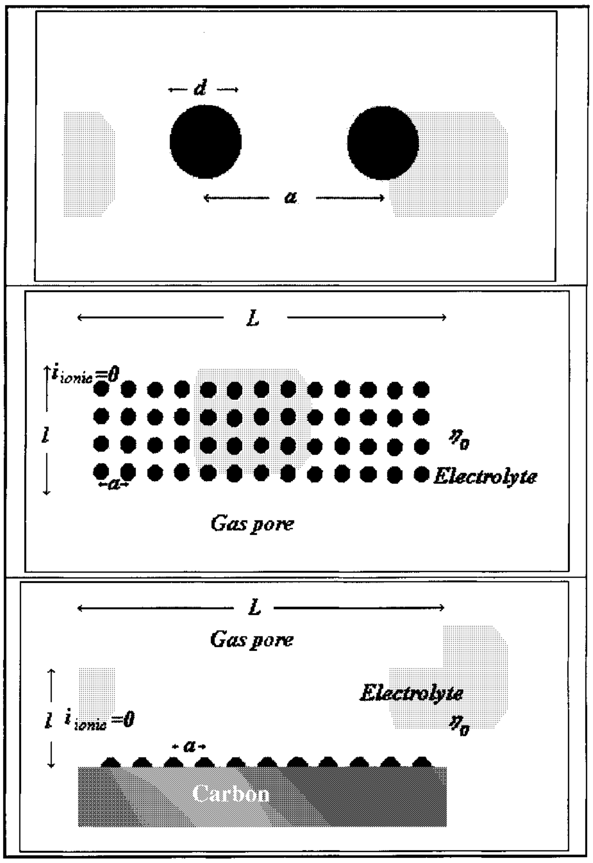
The homogeneous flooded model has demonstrated the practical benefits of using a thin catalyst layer because of the increase in the effectiveness factor with decreasing thickness of the active layer. However theory also points out other advantages resulting from the decrease of the ratio between the active surface area and the geometrical area of catalyst linked to an increase in the interparticle distance.

3. Mathematical model

3.1. *Geometry of catalyst arrangement*

The previous models did not take into account the fine structure of the active layer. In contrast, the aim of our work here is to develop a microscopic numerical approach to study the charge transfer in order to point out geometric effects on the ohmic drop at particle level in the same way as previously reported for mass transfer [3].

The local effects have been analysed using three models of systems presenting increasing complexity. The first model focuses on the competition effect between neighbouring particles in a system consisting of two isolated spheres located in the electrolyte (Fig. 1). The two other models are devoted to geometrical effects. The corresponding systems are hexagonal three-dimensional network of spherical particles in the electrolyte for the flooded agglomerate case (Fig. 2) and hexagonal two–dimensional network of hemispherical particles on a carbon plane for the thin film case (Fig. 3) [3].



Figs 1, 2 and 3. (Upper) Two isolated spheres. Competition between two particles. (Middle) Hexagonal 3D network of particles. Flooded agglomerate model. (Lower) Hexagonal 2D network of hemispheric particles. Thin film model.

3.2. *Basic equations*

In the presence of many gas pores inside the active layer, limitations by ionic ohmic drop through the active layer may become stronger than the diffusion limitations on which our previous studies were focused [2, 3].

Electrical charge conservation throughout the Nafion membrane leads to the Laplace equation in the absence of a proton concentration gradient:

$$\nabla(\kappa\vec{\nabla}(\Phi)) = 0 \tag{5}$$

The current is therefore calculated by solving this equation with the boundary conditions implied by symmetry and interface conditions:

(i) a Dirichlet condition can be formulated for the active layer–membrane interface:

$$\eta = \eta_0 \tag{6}$$

(ii) no ionic current can pass through any symmetry plan or through the gas–membrane interface:

$$i_{\text{ionic}} = 0 \tag{7}$$

(iii) a nonhomogeneous Neumann condition characterises the membrane–particle interface. The kinetics are assumed to be described by a Tafel law reduced to Equation 2(a) or 2(b):

$$i = i_o \exp(2.3\,\eta/b) \tag{8}$$

Note that the equations are identical to those describing pure diffusion when the kinetic law can be approximated by a linear relation, for which some results have been already published [3].

3.3. *Numerical solution*

The equations written in dimensionless form are solved using the finite element method with the commercial software FLUX-EXPERT®.

To implement the finite element method, Equation 5 is replaced by an integral form describing the electrolyte surface (Ω) using a projective function α according to Galerkin's method:

$$\iint_{\Omega} \alpha\nabla(-\sigma\nabla\Phi)\mathrm{d}S = 0 \tag{9}$$

The strong integral formulation can be replaced by a weak one by first decomposing the product of α and the divergence functions and then using the Green–Ostogradski theorem to restrict the divergence term to the boundary condition where it expresses the nonhomogeneous Neumann condition for the catalyst–particle interface. The identity between the ionic ohmic current at the particle–electrolyte interface and the charge transfer current makes it possible to take into account the Neumann and symmetry boundary conditions. A weak formulation is finally obtained:

$$\iint_{\Omega} \sigma\nabla\alpha\nabla\Phi\,\mathrm{d}S = \int_{\partial\Omega} \alpha(-\sigma\nabla\Phi)\,n\,\mathrm{d}l \tag{10}$$

Taking into account the boundary conditions, the right term of Equation 10 may be expressed as a function of the kinetic current density ($\partial\Omega$) which may in turn be expressed as a function of the overpotential at the particle interface:

$$\iint_{\Omega} \sigma\nabla\alpha\nabla\Phi\,\mathrm{d}S = \int_{\partial\Omega} \alpha i_o \exp(2.3\eta/b)\mathrm{d}l \tag{11}$$

This last equation can be used directly by FLUX-EXPERT® software. The classical finite element method is performed by approximating the projective function α and the unknown variable Φ using first and second orders polynomial functions.

3.4. *Dimensionless formulation*

When modelling charge transfer at the microscopic level of active layers, it is necessary to consider both electrochemical parameters (ionic conductivity κ, constants i_o and b of the interfacial kinetics law, total overpotential measured on the active layer η_o) and geometrical parameters (a, d, L, l as defined in Figs 1–3). The description of the problem under study therefore generally requires eight parameters expressed by three dimensions. Dimensional analysis can be used to obtain a dimensionless formulation with only

4 independent parameters and one dependent variable.

The dependent variable is the effectiveness factor, ε, which characterizes the electrocatalyst utilization. It is defined as the ratio of the experimental electrode current density to the maximal electrode current density, i_k, without limitations by ohmic drop and diffusion [11]:

$$\varepsilon = \frac{\text{experimental current density}}{\text{kinetic current density}} \atop \text{(without mass and ohmic limitations)}$$

$$= \frac{i}{i_k} \tag{12}$$

The four independent parameters to be considered are as follows:

(i) a geometrical dimensionless ratio (the ratio of the interparticle distance or the Nafion® layer thickness to the mean particle diameter): a/d, l/d or L/d;

(ii) the dimensionless ratio, V, as previously defined from Equation 4;

(iii) an equivalent characteristic ratio, v, related to the particle level:

$$v = 2.3\, i_o(d/2)/\kappa b \tag{13}$$

(iv) the dimensionless overpotential ratio (total overpotential measured on the active layer divided by the Tafel slope):

$$Y_o = 2.3\, \eta_o/b \tag{14}$$

In fact the dimensionless parameters V and v are the reciprocal of modified Wagner numbers, defined as the ratios of the resistance to charge transfer at the electrode and the ohmic resistance of the electrolyte to migration. Here these resistances vary over the width of the active layer as functions of the local overvoltage η and are considered close to equilibrium where the Tafel law can be approximated by a linear equation from a first order development and where the resistance to charge transfer remains constant.

4. Simulation conditions

The variation ranges for the dimensionless parameters V and v have been here mainly estimated from the values of electrochemical and geometrical parameters encountered in PEM fuel cells using platinum as an electrocatalyst. Nevertheless, the lack of accurate and consistent data for realistic working conditions of PEFMCs led us to consider a temperature close to 25 °C rather than within the range 70–90 °C.

The geometry of the active layer is complex and difficult to characterize in detail; consequently the geometric parameters (active and electrolyte layer thicknesses, mean particle diameter and specific surface area) can vary over wide ranges.

The dependence of mass activity on particle size implies using catalyst particle diameters ranging from 1 to 10 nm [12] for an interparticle distance varying between 1 and 40 nm [1]. The Nafion® layer can be characterized by a thickness from 100 nm to 1 μm [11]. The active area to geometrical area ratio γ ranges between 1 and 100 for both the thin film model and the flooded agglomerate model [11]. The ionic conductivity of the electrolyte depends on temperature and water content and can vary between 1 to 10 S m^{-1} [13] while the total overvoltage of the active layer is higher than $|300|$ mV at the cathode and lower than 150 mV at the anode.

Table 1. Kinetic parameters

Parameters	i_o/A cm^{-2}	b/mV dec^{-1}	η_0/mV
Oxygen reduction	10^{-10}	60–70	300–600
Hydrogen oxidation	10^{-3}–10^{-2}	30–120	< 150

For cathodic oxygen reduction, the kinetic parameters (exchange current density and slope of the Tafel line) are well known in the literature [13, 14]. For anodic hydrogen oxidation [15], on the other hand, they have been estimated only by a few works and so must be considered to vary over a wide range. These kinetic parameters are summarized in Table 1. Table 2 reports the resulting variation ranges for the dimensionless parameters used in the present study for each electrode.

5. Results and discussion

The numerical approach using finite element method was validated by comparing our present results to well-known results for some classical limiting cases (such as isolated catalytic spherical particles or planar ohmic drop).

5.1. *Case of two isolated spheres: competition effect between neighbouring particles*

The study of the competition effect between neighbouring particles is carried out for the case of two isolated particles. Simulation provides the variation of the effectiveness factor as a function of the geometric factor a/d (see Fig. 1) under mixed kinetic and ohmic drop control (characterized by parameters v and Y_o).

Under interfacial kinetics limitation (for example $v < 10^{-8}$, $Y_o < 18$), the effectiveness factor does not depend on the ratio a/d and it is close to unity. Under mixed kinetics and ionic ohmic drop limitation (e.g., $v = 10^{-8}$, $Y_o = 18$), the effectiveness factor

Table 2. Dimensionless parameters

Dimensionless parameters	V	v	Y_o
Oxygen reduction	3×10^{-15}–7×10^{-10}	3×10^{-15}–3×10^{-14}	9–18
Hydrogen oxidation	10^{-8}–10^{-2}	10^{-8}–10^{-5}	< 11.5

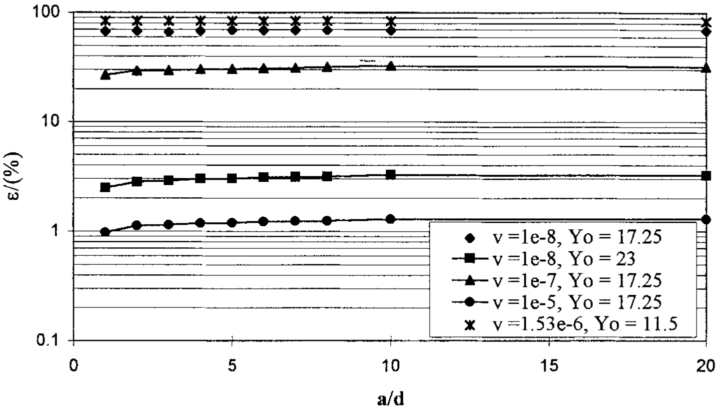


Fig. 4. Effectiveness factor for two isolated spheres against a/d under mixed kinetic and ohmic drop control.

decreases when a/d becomes smaller than 10. Moreover, the competition is increasingly important when the parameter Y_0 (i.e., the total overpotential η_0) increases, because in this case the interfacial kinetics rate also increases (Fig. 4).

Under ionic ohmic drop control it can be stated that the apparent specific activity decreases in a significant way when the interparticle distance becomes smaller than 10 times the particle diameter. A similar result was previously obtained for mass transfer limitation [2].

For oxygen reduction, the variation ranges for the dimensionless parameters v and Y_0 (Table 2) lead to ionic ohmic drops which are negligible related to electrochemical kinetics. On the other hand for hydrogen oxidation, the competition effect is significant. It may, therefore, be concluded that for oxygen reduction, the competition effect is always masked by kinetics while it may become significant for hydrogen oxidation.

5.2. *Case of hexagonal 3D network of spheres: flooded agglomerate model*

This second case is devoted to the ohmic drop limitations in a three-dimensional network of spherical particles. In fact the three-dimensional problem is reduced to two dimensions by considering that the six symmetry planes Π between two neighbouring particles define a cylinder with an axis Δ. First, Fig. 5 presents the potential distribution within a part of the active layer. The equipotential curves keep a quasi-linear shape with a slight curvature close to the catalyst particles.

Simulations point out the ionic ohmic drop limitation at the local level through the parameter v, or even at the whole active layer level through the parameter V. Moreover, they show that the competition effect depends on the geometrical ratio a/d as for the previous case of two isolated spheres.

Obviously, under kinetic control, the effectiveness factor does not significantly depend on either of the two dimensionless parameters (V, v) and remains close to unity. On the other hand, under mixed kinetic and ohmic drop control, computations with FLUX-EXPERT® and the classical model both indicate stiff decrease of the effectiveness factor as V increases (Fig. 6). In the same way, the effectiveness factor also decreases when the dimensionless parameter v increases (Fig. 7). These results demonstrate that a strong limitation on the active layer working behaviour is induced by the ionic ohmic drop, not only at the whole active layer level, but also at particle level. Consequently, a difference appears between our results and the previous predictions because local ohmic drop limitation at the particle level is not taken into account by the classical models (Fig. 6). Furthermore, for a quasiconstant value of V or v, the effectiveness factor decreases when other parameters decrease (Figs 6 and 7). Consequently, the ohmic drop limitation at particle level is added to the ohmic drop limitation within the Nafion® layer. This is the most striking result of these simulations. As for the first case, the ohmic limitation increases with parameter Y_0, that is, when the total overpotential, η_0, increases and the interfacial kinetics become faster.

A slight competition effect between neighbouring particles is shown in Fig. 8, under mixed kinetic and ohmic drop control, since the effectiveness factor steadily declines as neighbouring particles come closer together. Nevertheless, this competition effect (a/d) remains relatively small compared to the other effects (V and v).

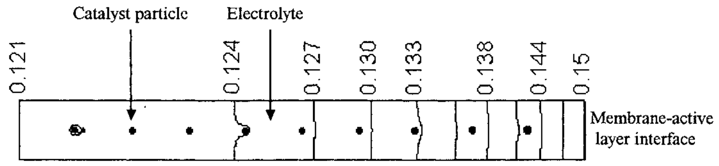


Fig. 5. Potential curves distribution in a part of active layer (anodic hydrogen oxidation).

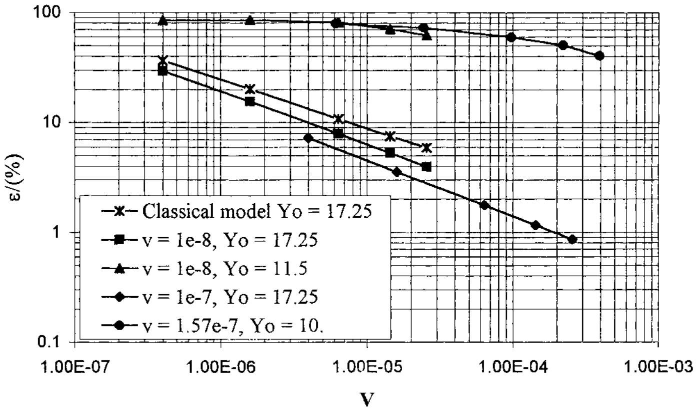


Fig. 6. Effectiveness factor for a hexagonal 3D network against parameter V ($v = Ct$, $a/d = 10$).

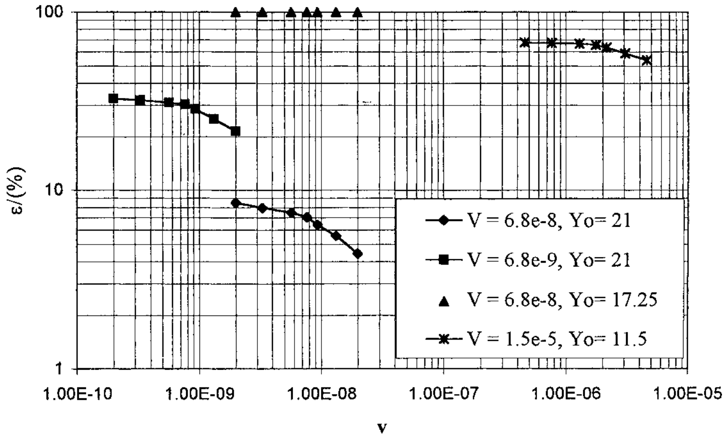


Fig. 7. Effectiveness factor for a hexagonal 3D network against parameter v ($V = Ct$, $a/d = 10$).

For oxygen reduction, ohmic drop limitation is almost negligible at the particle level, whereas it acts at the level of the whole active layer and can therefore reduce its efficiency. For hydrogen oxidation, obviously V and v slightly influence the active layer working behaviour, whereas the effect of parameter a/d remains negligible. These results are different from those obtained for the diffusion limiting case [3].

5.3. *Case of hexagonal 2D network of hemispherical particles: thin film model*

The aim of the study is to point out the effects of ionic ohmic drops, first through the Nafion® film (V) and secondly near catalyst particles (v), as well as the effect of competition between neighbouring particles (a/d), for different settings of the total overvoltage (Y_o).

Figure 9 shows that the conclusions obtained for a 3D network remain valid. First, the effectiveness factor, which has a constant value close to unity under kinetic control, decreases strongly under mixed kinetic and ohmic drop control as the parameters V or v increase. Secondly for almost constant values of parameter V, the effectiveness factor decreases if parameter v increases. Here again the ohmic drop limitation at the particle level is found to be added to the ohmic drop limitation within the Nafion® layer. Moreover, the effect of parameter Y_o is similar

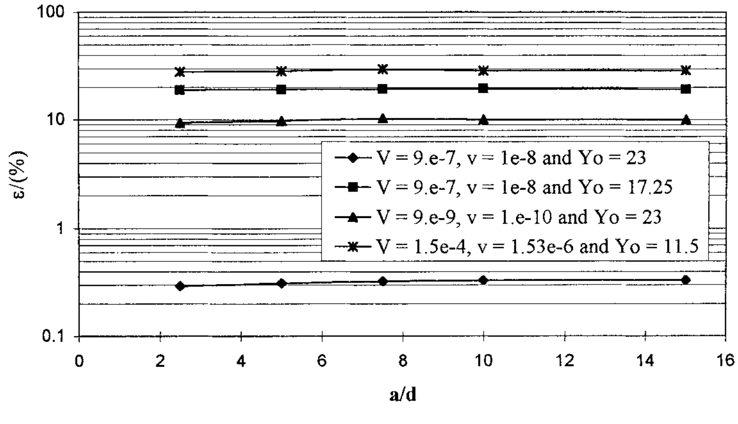


Fig. 8. Effectiveness factor for a hexagonal 3D network against a/d ($V = Ct$, $v = Ct$).

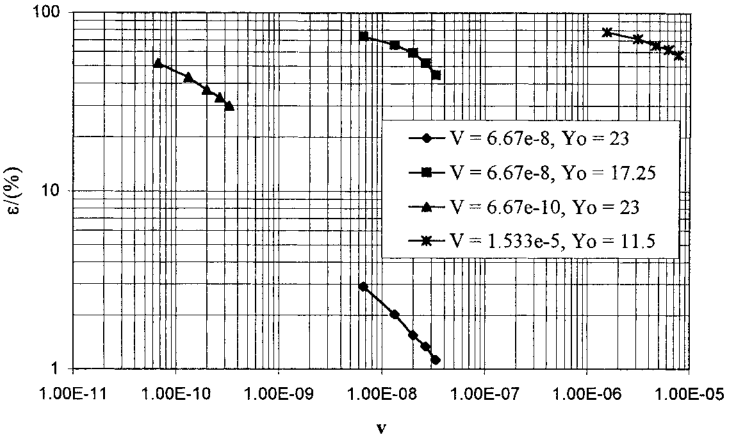


Fig. 9. Effectiveness factor for a hexagonal 2D network against v ($V = Ct$, $a/d = 10$).

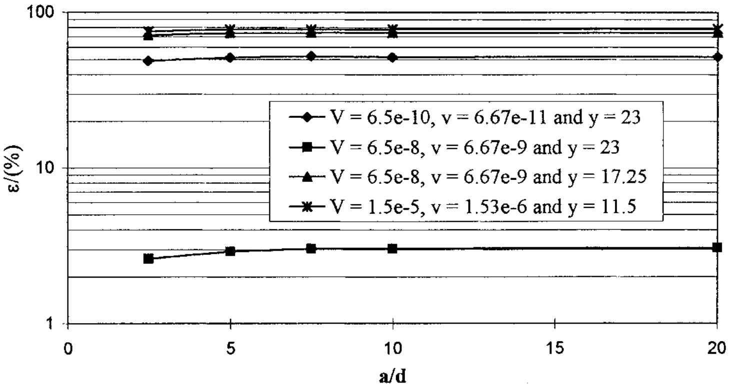


Fig. 10. Effectiveness factor for a hexagonal 2D network against a/d ($V = Ct$, $v = Ct$).

(Fig. 9) to that found in the previous case and a slight competition effect between neighbouring particles is also found for the thin film case under the same conditions as previously (Fig. 10). Generally speaking, the study leads to the same conclusions as for the flooded agglomerate case.

6. Conclusion

In this study, the effects of the local geometry of catalyst particle arrangement on ohmic drop within the active layer were pointed out and studied using dimensionless parameters.

The effect of competition of neighbouring particles (a/d) is masked under kinetic control and remains weak under mixed kinetic and ohmic drop control for an interparticle distance less than 10 times their diameter. More important, this study demonstrates the ionic ohmic drop limitation at the particle level (v) due to the discrete distribution of the catalyst as nano-particles. Moreover the results clearly show that this local limitation effect (v) must be added to the planar ohmic drop effect (V) considered in classical models. These effects pertaining to interfacial kinetics and ohmic drop through the Nafion® layer (V) or at particle level (v), both indicate the advantages obtained by reducing the electrolyte layer thickness (L) and the mean particle diameter (d), thereby decreasing limitation by the ohmic drop through the Nafion® or at the local level.

As a consequence, for an active layer presenting a high porosity, our simulations indicate that limitation by ionic ohmic drop is no longer negligible compared to diffusion. In such a case, it may be possible to improve performance by locating the catalyst particles close to the conducting proton membrane. For the opposite case of a non-porous layer, a distribution of the catalyst close to the gas inlet seems to be a better solution because of the strong limitation due to diffusion.

In further studies, we will present a microscopic approach to study the mass transfer within the active layer (diffusion and electrochemical reaction without ohmic drop limitation) in order to optimize both the geometry of the active layer and the distribution of catalytic nanoparticles.

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