STUDY OF MASS TRANSFER WITHIN THE ACTIVE LAYER OF P.E.M.F.C. ELECTRODES AT THE PARTICLE LEVEL.

Y. BULTEL¹, P. OZIL¹, R. DURAND¹, D. SIMONSSON².

1 Centre de Recherche en Electrochimie Minérale et en Génie des Procédés, URA CNRS 1212 - INPG, ENSEEG, BP 75 38402 St Martin d’Hères (France)
2 Dept of chemical Engineering and Technology, Applied Electrochemistry, KTH, S - 100 44, Stockholm (Sweden)

ABSTRACT

The present tendency is to increase the Pt/C ratio from 20% to 40% within the PEMFC layers and so new limitations on mass transfer could appear at the particle level. Four models presenting an increasing complexity are proposed in order to point out the geometrical effects on mass transfer. They show that the geometrical effect is masked at the cathode where oxygen reduction is limited by kinetics while hydrogen oxidation under diffusion control depends on the geometric characteristics of the active layer.

INTRODUCTION

Many projects in course are devoted to proton exchange membrane fuel cells (P.E.M.F.C.) which could be extremely attractive as a power source for space and terrestrial using. However the potential development of such a solution is strongly dependent on money savings to be performed for these systems. Among several keypoints, the technical ability of reducing the catalyst amount appears to be one of the main priorities. Therefore this work offers several complementary models at the particle level allowing to predict the behavior of the active layer. The goal to be reached should be a more efficient distribution of catalyst particles within the active layer from the basic knowledge of the local catalyst requirements.

CLASSICAL ACTIVE LAYER MODELS

The aim of this first part is to recall some classical models and experimental results presented in literature.

For a P.E.M.F.C. electrode, the kinetic current density related to the geometrical area is related to the specific activity $i^*$ by:

$$i_k = \gamma i^*(\eta) = W S i^*(\eta)$$

[1]
W being the catalyst loading, \( \gamma \) the ratio of the real surface area to the geometrical one and \( S \) the specific area which varies as \( d^{-1} \) for spherical or hemi-spherical particles. Then the mass activity (MA) is defined as:

\[
MA = S i^*(\eta) \tag{2}
\]

Numerous authors reported that the specific activity decreases for small Pt particles and thus obtained an experimental evidence of the particle size effect. The mass activity reach a peak value when the catalyst particle size is about 3 nm for O.R.R \((1)\). Consequently, the kinetic current density \( i_k \) is optimal when the mass activity is maximal, i.e. when the mean particle diameter \( d \) is about 3 nm.

The "experimental" current density \( i_{\text{exp}} = \varepsilon i_k \) can be optimized taking in mind the calculation of the effectiveness factor \( \varepsilon \) \((2)\) by the previous flooded model with the parameters relative to P.E.M. \((3)\).

In this relation, the effectiveness factor \( \varepsilon \) is considered to be defined as following:

\[
\varepsilon = \frac{\text{actual rate (current density)}}{\text{rate (current density) without mass and ohmic limitations}} \tag{3}
\]

So, if the ohmic and diffusion limitations are negligible, \( \varepsilon \) is close to unity and all the catalyst uniformly works in the porous electrode.

At the membrane-particle interface, the charge transfer flux density is expressed by:

\[
\varphi = \frac{i(\eta)}{nF} = k(\eta) \ C \tag{4}
\]

as a function of the kinetic constant \( k \):

\[
k(\eta) = \frac{1}{nF} \frac{di}{dC} \tag{5}
\]

The continuous flooded model takes into account that the reactant diffuses into the Nafion\(^6\) phase and simultaneously reacts at the catalyst interface. It was both admitted that the system is isothermal and under steady state conditions and that governing equations are reduced to a one-dimension form. At the electrode, a Tafel kinetics is assumed and all the coefficients are supposed to be constant in the active layer. Ionic conduction and diffusion are modelled using the Ohm's and Fick's laws.

For the totally flooded model, two characteristic dimensionless parameters can be defined:

\[
U^{-1} = \frac{\gamma k L}{D} \tag{6}
\]
For very high values of the ratio $U^/-/Wa^1$ such as in the usual case of P.E.M. (Nafion®), the active layer behavior is controlled by a strong diffusion limitation (much more important than the ohmic drop one). Then solving equations in respect of the boundary conditions leads to:

$$Wa^1 = \gamma \frac{\left( \frac{d\eta}{d\tau} \right)}{\sigma}$$  \hspace{1cm} [7]

Applying the flooded model leads to a theoretical increasing of the effectiveness factor when the active layer thickness $L$ decreases. This implies an advantage when using a thin P.E.M.F.C. layer (4), but also when the catalyst active surface area per geometrical area decreases and therefore when the interparticle distance increases. For other models with rather close gas pores, as the thin film model (5), the diffusion limitation is negligible in front of ohmic drops (very low $U^/-/Wa^1$ values), but nevertheless the effectiveness factor $\varepsilon$ decreases when $\gamma$ increases.

Whereas numerous works have indicated an effect due to the particle size, Stonehart (6) suggested that an other interparticle effect occurs at the local level. They evoke a mutual influence of particles on diffusion when they are close together. Then it is very important to check if the tendency of present researches consisting in increasing the Pt/C ratio from 10 to 40% (and consequently to decrease $L$) does not induce new limitations at the particle level.

MODELLING AT THE PARTICLE LEVEL

Definition of the physical problem

Several mathematical models have been developed for describing the behavior of the P.E.M.F.C. electrodes. All these models are classically based on the same description of the active layer structure: catalyst particles form porous aggregates which are flooded with electrolyte in the cell. In this way, a three-dimensional network of catalyst and electrolyte is present throughout the active layer. Moreover the carbon particles form a gas-filled network intermingled with the previous one and supplying gas throughout the active catalyst layer. The two major kinds of models proposed by literature are respectively the thin film model and the flooded model.

On one hand, the statement of the thin film model assumes that all the catalyst particles are located on the pore wall and that the thickness of the electrolyte film covering the whole pore is constant and very small compared to the pore size.
On the other hand the flooded model considers that the catalyst particles are uniformly dispersed within the electrolyte phase, so forming a continuous phase with the electrolyte phase. Obviously such models are not able to satisfactorily describe the spherical diffusion behavior in the neighboring of the carbon substrate nor to point out the interparticle distance effects. These lacks lead us to propose here a modelling at the particle level for predicting the behavior of the active layer.

In order to analyze the geometrical effects, four models concerning systems presenting an increasing geometrical complexity have been elaborated. The two first models are focused on isolated particles and the two other ones allow to consider the whole network of particles. In a more accurate way, the first model is devoted to two isolated particles while the second one concerns a fraction of an isolated particle disposed on a carbon plane. The third model is a thin film model developed from the particle level by considering a two-dimensional hexagonal network of hemispherical particles under a thin film layer of electrolyte. Finally the last model is a flooded model based on a description at the particle level for a three dimensional network (Figure 1).

In spite of the geometrical differences, the same following hypotheses were assumed for the four systems under study:
- the catalyst particles are spheres having the same mean diameter and moreover for models 3 and 4, they are steadily distributed within the electrolyte phase according to an hexagonal network,
- ohmic drops limitation are negligible in front of the mass transfer limitation and all the transfer coefficients are looked as constant in the neighboring of the substrate,
- The kinetic rate equation for the electrochemical reaction on the particle active surface is described by a Tafel law and it is a first order vs the activity of the gaseous reactant. Thus the transfer current density is given by:
  \[ i = i_0 \exp \left( \frac{2.3 n}{b} \right) \frac{C}{C_0} \]  
while the reaction rate for the gas reactant is expressed as: \( \varphi = \frac{j}{nF} \).
- At the particle level, overpotentials are assumed to be constant because the characteristic dimensions are small compared to the electrode size and consequently the mass transfer coefficient is also constant.

Formulation of the problem

The modelling depends on a lot of variables such as geometrical parameters (interparticle distance, particle diameter), transfer characteristics (diffusion coefficient, mass transfer coefficient, ionic conductivity), reactant concentration and flux density. A dimensionless formulation is suitable for describing in the most general way the problem under study.
This is done by defining the following variables:

- the dimensionless flux density (mean calculated flux density referred to the particle active surface area in reference to the flux density for an isolated spherical particle):

\[
\frac{\varphi}{DC_0(d/2)} \tag{10}
\]

- the dimensionless ratio between charge transfer and ohmic resistances (Wagner number):

\[
w_a = \frac{\sigma}{(d/d_1) d/2} \tag{11}
\]

- the dimensionless ratio of spherical diffusion and charge transfer flux densities (inverse of a modified Damköhler number):

\[
u = \frac{D}{k(d/2)} \tag{12}
\]

- the dimensionless geometric ratio between the interparticle distance and the particle diameter: \(a/d\)

At the particle level, the active layer behavior can be summarized as following. The electroactive species diffuses throughout the thin film of Nafion\(^\text{®}\) electrolyte from the gas-membrane interface where gas dissolution occurs to the membrane-particle interface where gas reacts. Diffusion within the electrolyte thin layer is controlled by the Laplace equation \([13]\) and the concentration at the gas-membrane interface is imposed at a constant value while the reactant is consumed at the membrane-particle interface.

The resolution of the dimensionless equation is performed for spherical particles with the commercial software FLUX-EXPERT\(^\text{®}\) by using the finite elements method. Subsequently the mass transfer flux density can be deduced by solving the Laplace equation in respect to the following boundary conditions.

All the geometrical systems under study present an axial symmetry. For the two last systems, symmetry is not so obvious as for the two first ones. In fact, six symmetry planes are to be considered between a given particle and its neighboring, so implying an hexagonal symmetry which can be approximated by a cylindrical symmetry. As a result, the dimensionless equation can be rewritten in terms of cylindrical coordinates by using axisymmetric conditions for any variable \(X (\partial X/\partial \theta = 0)\).
Then the Laplace equation:

$$\nabla^2 C = 0$$  \[13\]

is reduced to:

$$\frac{1}{r} \left( r \frac{\partial^2 C}{\partial r^2} \right) + \frac{\partial^2 C}{\partial z^2} = 0$$  \[14\]

and has to be solved with the following boundary conditions:

- Dirichlet condition at the gas-membrane interface

$$C = C_0$$  \[15\]

- non homogeneous Neumann condition at the membrane-particule interface

$$\varphi = k C_i$$  \[16\]

The mean flux density computed at the membrane-particle interface is calculated with:

$$\bar{\varphi} = \frac{\int_{\partial S} \varphi \, dS}{S}$$  \[17\]

where \(S\) is the usable particle active surface area.

RESULTS AND COMMENTS

As a preliminary study, the numerical approach using finite element method was validated by comparing the obtained solutions to the well-known ones established in some classical limiting cases for heat transfer. The analogy between heat and mass transfers is obvious owing to the similarity of both Laplace equations and boundary conditions leading to formally equal heat flow and mass transfer densities in a same geometrical system. In order to compare and to validate the numerical solution, two limiting cases leading to the analytical solutions (see appendix) were considered here.

The dimensionless flux density calculated by the software for highest values of the ratio \(a/d\) under diffusion control tends to unity, value forecasted by the analytical solution in the case of two isolated particles located in an infinite medium (Figure 2) and characteristic of a spherical diffusion. Moreover, for well dispersed catalyst particles \((a/d>10)\) under a thin film of electrolyte \((e/d=10-20)\), the computed flux density tends to the values predicted from the analytical solution (case of an isothermal sphere located in a semi-infinite medium limited by an isothermal surface) (figure 4).

As shown by figures 2 and 4, the results obtained from the numerical method proposed here with axisymmetric conditions are in a good agreement with the analytical solutions. Thus the selected computing method appears to be suitable for determining the flux density in the systems under study.
Case 1

For two isolated particles flooded in the Nafion® electrolyte under a mixed diffusion and kinetic control, solving the dimensionless equation allows to deduce the mean flux density as a function of the dimensionless $a/d$ and $u$ parameters. Then it becomes possible to estimate the effect of interparticle distance (related to the diameter particle) on the flux density as shown by figure 2.

If the system is under kinetic limitation ($u < 10^2$), the dimensionless flux density does not depend on the geometrical ratio $a/d$, so proving that the interparticle distance $a/d$ has no effect. However when diffusion becomes predominant, the flux density clearly depends on parameter $a/d$. Namely, it strongly decreases from a plateau value when $a/d$ becomes smaller than 10.

As a conclusion, it can be stated that under diffusion control, when the interparticle distance becomes smaller than 10 times the particle diameter, the apparent specific activity significantly decreases.

Case 2

The second geometrical case concerns a fraction of particle disposed on a carbon plane under a thick Nafion® layer. Diffusion limitation will be only considered here. The aim of this study is to point out the effect of the contact angle $\theta$ between the carbon substrate and the particle in order to estimate the corner effect.

It appears that if the contact angle is equal to $90^\circ$ corresponding to the case of one hemispherical particle, the dimensionless flux density is the same as for an isolated sphere, so showing that there is no noticeable effect of the substrate. Nevertheless, when the contact angle decreases down to $0^\circ$, the dimensionless flux density slightly decreases.

So there is an effect due to the contact angle between the particle and the substrate, although the corner effect remains smaller. This fact clearly establishes that the entire particle active surface area is not available.

Case 3

The purpose of the third case is to study diffusion toward a two-dimensional network of hemispherical particles under a thin film layer for a mixed diffusion and kinetic control. Here the flux density is again computed as a function of parameters $u$ and $a/d$ as shown on figure 3.

On one hand, under kinetic limitation as for the first modelling, the flux density does not depend on the interparticle distance and thus no more on the catalyst loading. Otherwise it is noticed that kinetics mask the whole geometrical effect. On the other hand, if diffusion becomes predominant, the flux density depends on the loading and the geometric effects are quite the same as for two isolated particles. When the
dimensionless ratio \( a/d \) decreases from 10, the flux density strongly decreases while it remains constant for \( a/d \) values higher than 10 (figure 3). Nevertheless, the most important point is that the flux density is the same as for an isolated sphere for the large values of \( a/d \), while the effective diffusion is close to planar diffusion for small values of \( a/d \) (figure 4). Consequently it appears not only an interparticle distance effect but moreover a concentration diminution due to the increasing of catalyst loading on the surface.

To conclude about the interparticle effect, such an effect is easy to be explained. On one hand, when a particle is well separated from the neighboring particles, then the full active surface area is available for the reactant which is undergoing to a spherical diffusion to the individual particles. On the other hand, if the particles are close together within some critical region, a mutual influence on diffusion occurs, so limiting the available active surface area.

Case 4

The three previous systems provide interesting information concerning the mass transfer, but their major inconvenient is a relevant description limited to the neighboring of the substrate and consequently to very thin layers. So a more realistic geometric model is required for modelling the behavior of the active layers. Such a modelling is possible from a three dimensional hexagonal network of particles, the symmetry of which allows again a two-dimension mathematical treatment. Moreover the results forecasted from this modelling can be compared to the flooded model and to a modified flooded model which takes into account the local spherical diffusion in the particle vicinity (see appendix). The comparison between these three models is described by figure 5 from the evolution of the effectiveness factor with parameter \( \text{u} \).

If kinetics are predominant (\( \text{u}>10^2 \)), no difference appears between the results provided by the three models. In opposition when diffusion becomes the limiting step (\( \text{u}<10^{-2} \)), similar predictions are only obtained from computations with FLUX-EXPERT® and analytic calculations from the modified flooded model which both conclude to a stiffer decreasing of the effectiveness factor than with the flooded model. This strong difference is due to the fact that the local geometry is not taken into account for stating the classical flooded model while actually the accumulation of catalyst under a particle form induces a spherical diffusion limitation and probably a shielding effect of particles).

A parametric study performed with the FLUX-EXPERT® software, shows that, if the layer active thickness \( L \) or the real surface area / geometric area ratio \( \gamma \) increases the effectiveness factor \( \varepsilon \) decreases as forecasted by the flooded model (figures 6 and 7) as the results given by the flooded model. In other respects, for constant values of \( L \) and \( \gamma \), the effectiveness factor \( \varepsilon \) increases if interparticle distance \( a \) increases (figure 8) due to the diminution of the mutual interaction between particles.
CONCLUSIONS

This study demonstrates an geometrical effect on the flux density due to the interparticle distance, the corner effect and the catalyst loading. This effect acts as a function of the dimensionless parameter \( u = 2 \frac{D}{k} \cdot d \).

If considering the concrete case of oxygen/hydrogen fuel cells, the oxygen reduction is controlled by kinetics \((u<10^2)\), thus the geometrical effect is masked at the cathode. However, the hydrogen oxidation is controlled by diffusion \((u<10^{-2})\) and so depends on the geometric characteristics of the active layer. Consequently the tendency to increase the Pt/C ratio induces new limitations at the particle level only for the anode.

NOMENCLATURE

\begin{itemize}
  \item \( a \) interparticle distance (m)
  \item \( b \) Tafel slope (V.dec^{-1})
  \item \( C \) concentration in the electrolyte phase (mol.m^{-3})
  \item \( d \) mean particle diameter (m)
  \item \( D \) diffusion coefficient within the electrolyte phase (m^{2}.s^{-1})
  \item \( e \) layer thickness (m)
  \item \( F \) Faraday constant (96500 C.mole^{-1})
  \item \( i \) current density (A.m^{-2})
  \item \( k \) kinetic constant (m.s^{-1})
  \item \( L \) active layer thickness (m)
  \item \( n \) total number of electrons involved in the electrochemical reaction
  \item \( S \) catalyst specific area (m^{2}.kg^{-1})
  \item \( W \) catalyst loading (kg.m^{-2})
  \item \( \gamma \) real catalyst area / geometric area ratio (m^{2}.m^{-2})
  \item \( \eta \) local overpotential (V)
  \item \( \varphi \) flux density (mole.m^{-2}.s^{-1})
  \item \( \sigma \) ionic conductivity within the electrolyte phase (S.m^{-1})
  \item \( \theta \) contact angle between the particle and the substrate (°)
  \item \( i \) index referring to the electrolyte membrane-particle interface
  \item \( o \) index referring to the gas-electrolyte interface
\end{itemize}

APPENDIX

Appendix 1: Analytical solution for an isothermal sphere buried in semi-infinite medium having an isothermal surface (7):

The heat flow density \( \varphi \) is given by:

\[ \varphi = \frac{K \Delta T}{d/2} \left( \frac{1}{1 - d/4e} \right) \]  \[18\]
where $K$ is the thermal conductivity, $\Delta T$ the temperature difference and $e$ the distance between the sphere center and the isothermal surface.

By analogy the mass flow density is expressed form the concentration difference $\Delta C$ as:

$$\varphi = \frac{D \Delta C}{d/2} \left( \frac{1}{1 - d/4e} \right) \quad [19]$$

**Appendix 2:** Flooded model and modified model equations:

For the flooded model, the flux density is defined by the relationship:

$$\varphi = \frac{D C_0}{Z_d} \tanh \left( \frac{L}{Z_d} \right) C_0 \quad [20]$$

with $Z_d = \sqrt{D/K}$, where $L$ is the active layer thickness of electrolyte and $K (s^{-1})$ the reaction rate constant for a first order reaction.

The one final difference between the classical flooded model and the modified one consists in using a modified reaction rate constant $K$ including local spherical diffusion expressed as (8):

$$K = \frac{\gamma k}{L} \left( \frac{2 D}{k + 2 D} \right) \quad [21]$$

instead of:

$$K = \frac{\gamma k}{L} \quad [22]$$

**REFERENCES**

1. A. Kabbabi and al., Electroanal. Chem., 373, 251 (1994); A. Gamez and coll., Electrochem Acta. (under press)
2. P. Stonehart, P. Ross, Electrochim. acta., 21, 441 (1975)
3. F. Gloagen, PhD Thesis, Grenoble (1994)
4. M. S. Wilson, S. Gottesfield, J. Electrochem. Soc., 199, L 28 (1992)
5. S. Srinivasan, H. D. Hurwitz, Electrochim. Acta., 46, 495 (1992)
6. M. Watanabe, H. Sei, P. Stonehart, J. Electroanal. Chem., 261, 375 (1981)
7. J. P. Holman, Heat transfer, McGraw-Hill, p. 80, New York (1990)
8. C. Parascandola, Trinity College Report, Dublin (1993)
| CASE 1 | Two isolated particles both diffusion and kinetic control |
|--------|----------------------------------------------------------|
| CASE 2 | Contact between particles and substrate diffusion control |
| CASE 3 | Hemispheric particles within an hexagonal 2D network diffusion control |
| CASE 4 | Spherical particles within an hexagonal 3D network both diffusion and kinetic control |

Figure 1: Geometrical case under study

Figure 2: Dimensionless flux density to 2 isolated spherical particles vs. dimensionless geometrical ratio under mixed diffusion and kinetic control.
Figure 3: Dimensionless flux density to a 2D hexagonal network of spherical particles vs. dimensionless geometrical ratio under mixed diffusion and kinetic control.

Figure 4: Dimensionless flux density to a 2D hexagonal network of hemispherical particles vs. dimensionless geometrical ratio under diffusion control.
Figure 5: Effectiveness factor for the same active layer ($L=200 \text{ nm}$, $\gamma=3,12 \text{ m}^2\text{.m}^{-2}$) and a 3D hexagonal network of particles ($d=2 \text{ nm}$) vs. dimensionless parameter $u$.

Figure 6: Effectiveness factor for a 3D hexagonal network of particles ($d=2 \text{ nm}$, $\gamma=6,3 \text{ m}^2\text{.m}^{-2}$) vs. dimensionless parameter $u$ and active layer thickness $L$. 
Figure 7: Effectiveness factor for a 3D hexagonal network of particles ($L=200$ nm, $d=2$ nm) vs. dimensionless parameter $u$ and real catalyst area/geometric area ratio $\gamma$.

Figure 8: Effectiveness factor computed to a 3D hexagonal network of particles ($L=400$ nm, $\gamma=6.3$ m$^2$/m$^2$) vs. dimensionless parameter $u$ and for 10, 16, 40 nm.