Modelling of the gas-phase mass-transfer resistance at PEMFC electrodes

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The mass-transfer phenomena at the electrodes and, in particular, the diffusion of oxygen at the cathode significantly affect the limit performance of PEMFCs. Some particular geometric arrangements, such as the interdigitated or serpentine, have demonstrated their effectiveness in lowering diffusive resistances.

It is possible to have a better understanding of these phenomena by determining the various possible diffusive regimes taking place inside the porous layer close to the electrodes. In each regime the interaction between the diffusive and forced flows can be expressed in terms of Peclet number and the overall diffusive resistance in terms of Sherwood number.

In this way, the comparison of traditional and non-traditional geometric arrangements can be studied in greater detail, so that the problems relating to the simulation and optimisation of the cell can be more efficiently dealt with.

A model of the gas-phase mass-transfer resistance at PEMFC electrodes has been set up and in this paper a comparison of an approximate and a numerical solution for the model will be presented; the results of the two different approaches show good agreement in terms of limit regimes.

1. Introduction

The important role of mass-transfer phenomena, and in particular of the diffusion of oxygen at the cathode, in lowering the limit performance of polymeric membrane fuel cells (PEMFCs) is now universally known.

To better understanding these phenomena (Arato and Costa, 2006a) it is useful to distinguish the various possible diffusive regimes taking place inside the porous layer close to the electrodes; by expressing the interaction between diffusive and forced flows in terms of Peclet numbers and the overall resistance in terms of Sherwood numbers, which are, in turn, a function of the Peclet number, three regimes can be defined. This preliminary approach, based on a simplified physical-mathematical description and its analytical solution, has been shown to be effective in explaining some of the important differences in the performance of different cell geometries, both traditional and non-traditional, especially in terms of the limit current.

Both interdigitated (Sukkee and Wang, 2004, Yi and Van Nguyen, 1999) and serpentine (Zhukovsky and Pozio, 2004) cells can be operated at high Sherwood numbers, corresponding to high limit currents, but both are correspondingly penalised by higher head losses then traditional cells.

The approximate results (Arato et al., 2006b) of the analytical solution can be useful for comparing the various geometric arrangements and their simulation and optimisation problems.

On the other hand, a rigorous estimation of the Sherwood number (Arato et al., 2007) is useful for obtaining a detailed description of the electrochemical kinetics and a more reliable comparison of the different channel geometries.

2. The Model

Making reference to a couple of parallel channels and to a porous layer through which the reaction gas has to migrate and diffuse before reaching the reaction site on the electrode, the spatial domain considered, shown in Figure 1, has a rectangular *h(b+d)* section.

The diffusion and migration phenomena in the partial *hd* domain can be described according to the differential equation (Zhukovsky and Pozio, 2004):

$$-\rho D\left(\frac{\partial^2\omega}{\partial x^2}+\frac{\partial^2\omega}{\partial y^2}\right)+\rho v\frac{\partial\omega}{\partial y}=0 \qquad 0<\mathrm{y}<\mathrm{d}\ ,\ 0<\mathrm{x}<\mathrm{h} \tag{1}$$

The assumed simplifying hypotheses are:

- Steady state, as the diffusion times of the porous layer are less than 1s;
- Two-dimensional geometry;
- Uniform properties in the gas phase, assuming that the variation in temperature and pressure can be considered negligible and a dilute gas phase;
- Viscous regime inside the porous medium, as the Reynolds numbers of the medium itself are normally lower than unity;
- Instantaneous reaction at the electrode surface, which corresponds to limit current conditions;
- Null orthogonal velocity at the boundaries, which implies, among other things, an instantaneous reaction on the electrode surface.

To calculate the migration velocity a simple integrated form of the Darcy equation for incompressible fluid

$$v=\frac{k(P_1-P_2)}{\mu d} \tag{2}$$

is sufficient; in fact, as the pressure differences are low, the flow field can be assumed to be uniform and h<<d.

3. The Approximate Solution

3.1 The Limit Regimes

The limit regimes taking place inside the porous layer close to the electrode can be defined (Arato and Costa, 2006a) by comparing the axial and the transversal diffusion times (along the y and x axes respectively) to the residence time inside the porous medium itself.

In this way we obtain two dimensionless parameters, such as the axial Peclet number and the transversal Peclet number, with reference to which the role of the diffusive phenomena is discussed.

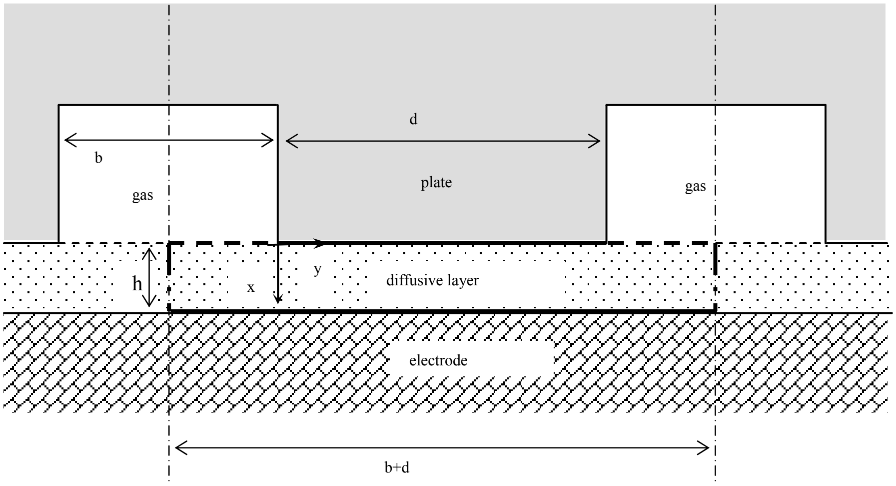

Figure 1: The spatial domain considered

As d>>h normally, it can assumed that $Pe_x << Pe_y$, so we principally refer to this equation. In particular, when $Pe_y << 1$ the regime close to the electrode can be considered purely diffusive and the reagent flux depends on the mean driving force and is independent by the velocity; when $Pe_y >> 1$ a forced regime must be considered and the effects of axial diffusion can be neglected when compared to the forced migration. Moreover, two forced sub-regimes can be considered: a flow rate-controlled regime, characterised by $Pe_y >> 1$ and $Pe_x << 1$, in which case the flux to the electrode is directly proportional to the velocity, and a pellicular-forced regime, characterised by $Pe_y >> 1$ and $Pe_x >> 1$, in which case the flux to the electrode is proportional to the square root of the velocity. In the first sub-regime the entire reagent reaches the electrode, while in the second the residence time is too short for the transversal diffusion times, so that only the reagent in a thin pellicular layer near the electrode can be consumed.

The ratio of the calculated flux and a reference flux, corresponding to the diffusion in the homogeneous gas phase of a square section *bb* of a channel, defines the Sherwood number. Obviously, for a complete analysis, the area under the channels must also be considered, above all in the case of pure diffusion. In such a way, we can obtain (Arato et al., 2006b) a constant value of the Sherwood number for the first limit regime considered; for the flow-rate forced regime the Sherwood number is directly proportional to the transversal Peclet number; while for the pellicular-forced regime the Sherwood number depends on the square root of the transversal Peclet number.

In Figure 2 the dependence of the Sherwood number on the transversal Peclet number for the three limit regimes is reported.

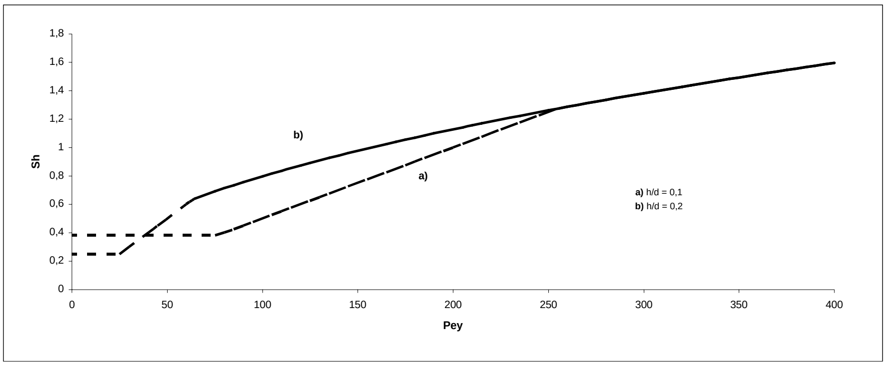

Figure 2: An example of dependence of Sh on Pey

4. The Numerical Solution

A rigorous calculation of the Sherwood number (Arato et al., 2007), which quantifies the mass transfer resistances close to the electrode, was performed using a Fortran code, which calculates the flow field, the composition field and the overall flux to the electrode, with a relaxation convergence method.

In the case of a parallel-channel configuration, such as the one typically used in interdigitated cells, the calculated flow field shows some symmetry properties, such as the absolute value of velocity as reported in Figure 3.

Figure 4 represents an example of a calculated composition field. The mean thickness of the “exhaust” layer close to the electrode depends on the mean migration velocity and becomes finer as the velocity increases.

Finally, in order to describe the composition field in terms of a Sherwood number, it is possible to calculate the $Sh(Pe_y)$ function. The comparison of this curve and the approximate curve is reported in Figure 5.

5. Conclusions

To obtain a detailed and accurate description of the electrochemical kinetics and so a more reliable comparison of the various geometric arrangements used for the distribution of the reactants, it is necessary to calculate the Sherwood number in a rigorous way.

In fact, as already discussed in other works, both interdigitated and serpentine cells can operate at high Sherwood number, corresponding to high limit currents, even if both are penalised by higher head losses than traditional cells, so a better understanding of this features can help in obtaining a geometric optimisation of the cell. On the other hand, the comparison of the solutions of the approximate approach and the results of the numerical ones in terms of flow regimes shows good agreement.

For a preliminary estimation, therefore, the former approach is substantially accurate and particularly useful.

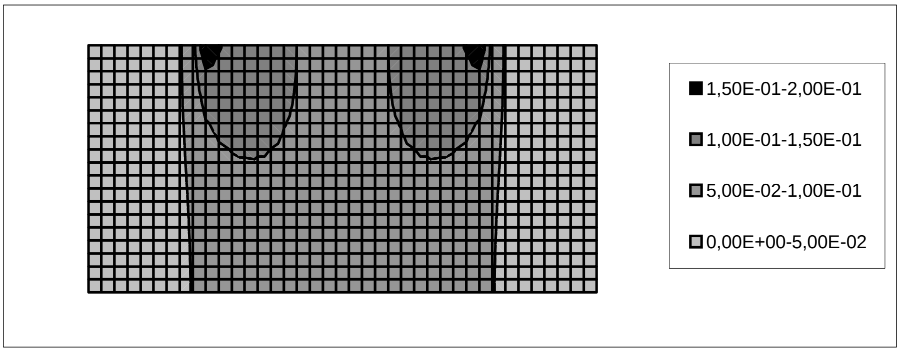

Figure 3: The absolute value of the reduced velocity field for $Pe_y=100$.

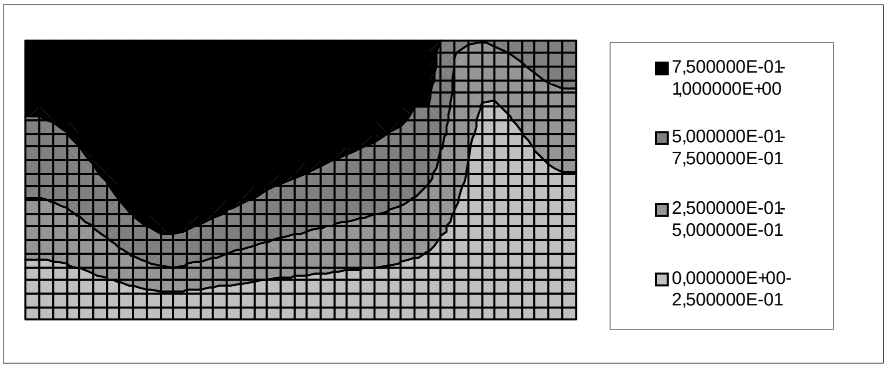

Figure 4: The reduced composition field for $Pe_y=300$.

6. Symbols

b	width of channel	[m]
d	length of the diffusive layer	[m]
D	effective diffusivity in the porous medium	[m^2s^{-1}]
h	thickness of the diffusive layer	[m]
k	permeability of the porous medium	[m^2]
P	absolute pressure	[kg $m^{-1}s^{-2}$]
Pe	Peclet number	[-]
Sh	Sherwood number	[-]
v	velocity in the porous medium	[m s^{-1}]
x	spatial co-ordinate, perpendicular to the electrode	[m]

y	spatial co-ordinate, parallel to the electrode	[m]
μ	viscosity of the gas	[kg $m^{-1}s^{-1}$]
ρ	density of the gas	[kg m^{-3}]
ω	mass fraction	[-]

subscript

x	x-axis, perpendicular to the electrode
y	y-axis, parallel to the electrode
1	channel 1
2	channel 2, adjacent to channel 1

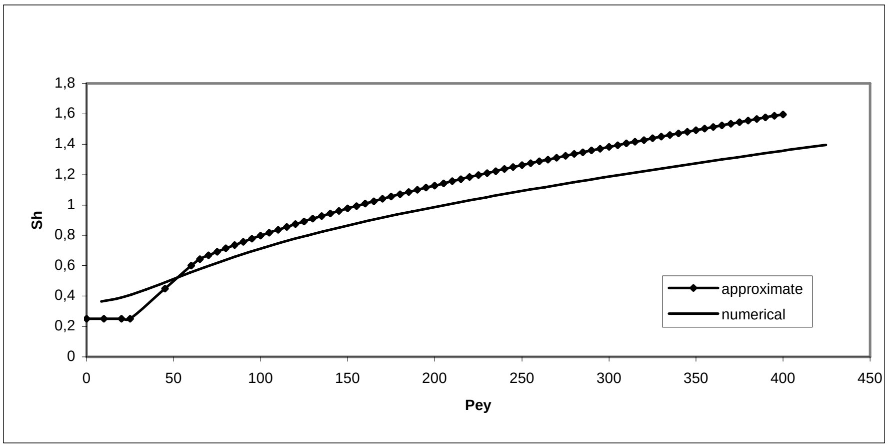

Figure 5: Comparison of the approximate and numerical solutions.

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