

Transport phenomena in membranes for PEMFC applications: an analytical approach to the calculation of membrane resistance

M. De Francesco*, E. Arato, P. Costa

Dipartimento di Ingegneria Ambientale, Università di Genova, Via Opera Pia 15, 16145 Genoa, Italy

Received 13 February 2003; received in revised form 10 November 2003; accepted 26 January 2004

Abstract

The transport phenomena of mass and electrical charges play an important role in the proton exchange membrane utilised in fuel cell applications. The calculation of the membrane ion and water transfer is usually determined in two ways: one is a semi-empirical mode that can be experimentally set for any application and cannot be used in the prediction of the characteristics of new cells, and the other is a very complex mathematical approach that needs very long calculation times. In fact, the membrane mass transfer model can cause problems in the management of PEM stack models, by increasing calculation times and, above all, convergence problems. This work attempts to overcome this bottleneck using a novel approach. The validation of the new approach has been made by applying the model results to a PEM fuel cell model and by comparing the overall results to those in the literature. The resulting calculation time warranted the application of this model to a very complex stack simulation, resulting in good fit and reasonable computing times.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Fuel cells; Proton exchange membrane; Membrane ion transfer; Nafion® membrane

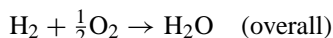
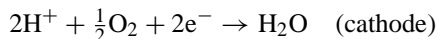
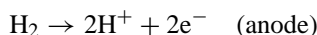
1. Introduction

In fuel cell the direct conversion of the chemical energy of the reactants to electrical energy is achieved with high efficiency and high environmental compatibility [1]. Among the different types of fuel cells, proton exchange membrane fuel cells (PEMFC) are now considered the best solution for automotive applications [1–7]. This is due to the flexibility of their use (starting is very simple, the device is of small dimensions, efficiency is very good) and their low working temperature, which is important for the intrinsic safety of the vehicle. For these applications, the modelisation of the stack is needed to proceed to the definition of the overall vehicle design. In particular [5] the use of a dynamic model can be considered the basis for the successful assembling of all the power devices (stacks, feeder, batteries, utilizers). The dynamic response can be pursued only if the stack model does not need high calculation times and in this case some simplifications may be necessary [5] in the calculation of membrane conductivity, an intrinsic property of PEMFCs.

These cells consist of a perfluorosulfonic membrane electrolyte coupled with two electrodes (anode and cathode) made of a substrate of carbon-PTFE coated with platinum as electrocatalyst, as schematised in Fig. 1.

Air is fed to the cathodic compartment while hydrogen is fed to the anodic one and the electrolyte performs the functions of transferring H^+ from the anode to the cathode and separating gaseous reactant. In particular, the H^+ transfer can be realised only when the membrane is strongly hydrated [5].

Electrochemical reactions involved are:



Stacks are obtained by connecting a number of cells in series with gas distributors (bipolar plates) that feed the fuel to the anodic side and the oxidant to the cathodic one.

As mentioned above, hydration level conditions the proton transfer (or proton conductivity) in the membrane. In fact, the sulfonic groups easily dissociate into SO_3^- and H^+ in these membranes in the presence of water. Under this condition, the proton can be considered as a mobile charge that encounters a low resistance when moving across a potential gradient. To achieve the membrane humidification,

* Corresponding author. Tel.: +39-010-353-6502;

fax: +39-010-353-2589.

E-mail address: mdf@diam.unige.it (M. De Francesco).

Nomenclature	
a	air relative humidity, dimensionless
C_i	concentration of “ i ” (mol m^{-3})
C_{is}	dry ionic concentration of “ i ” (mol m^{-3})
D_i	diffusivity of “ i ” in the membrane ($\text{m}^2 \text{s}^{-1}$)
D_λ	diffusivity in the hydrated membrane defined by Eq. (2) ($\text{m}^2 \text{s}^{-1}$)
e	humidification parameter, dimensionless
F	Faraday constant (C mol^{-1})
I	electrical current density (A m^{-2})
j	adimensional current, defined by Eq. (21)
J	total flux of ions ($\text{mol m}^{-2} \text{s}^{-1}$)
J_i	flux of “ i ” ($\text{mol m}^{-2} \text{s}^{-1}$)
k	hydraulic permeability of the membrane (m^2)
k_b	Boltzmann constant ($\text{J mol}^{-1} \text{K}^{-1}$)
m	membrane thickness (m)
M	equivalent weight of membrane, i.e. weight of membrane/mol of SO_3^- groups (g mol^{-1})
n	adimensional total water flux, defined by Eq. (21)
n_c	number of electrons transferred in the reaction, dimensionless
P	total pressure (Pa)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
s	membrane thickness in dry conditions (m)
T	temperature (K)
V	potential (V)
V_i	molar volume of “ i ” ($\text{m}^3 \text{mol}^{-1}$)
x	geometrical coordinate along the membrane (m)
x_s	geometrical coordinate along the dry membrane (m)
y	adimensional geometrical coordinate defined by Eq. (17)
y_i	molar fraction of “ i ”
z_i	electric charge of “ i ”
<i>Greek letters</i>	
α	parameter defined by Eq. (30), dimensionless
β, β', β''	parameters defined by Eq. (22), dimensionless
γ	parameter defined by Eq. (21), dimensionless
$\gamma_1, \gamma_2,$ γ_3, γ_4	coefficients in Eq. (3)
γ'_1, γ'_2	coefficients in Eq. (32)
δ, δ'	parameters defined by Eq. (22), dimensionless
ζ	electro-osmotic drag coefficient, dimensionless
η	adimensional membrane tension
θ	diameter of water molecule (m)
λ	membrane hydration, i.e. the ratio $\text{H}_2\text{O}/\text{SO}_3^-$ in membrane, dimensionless
π	adimensional pressure
ρ	membrane density (kg m^{-3})
σ	resistivity ($\Omega^{-1} \text{m}^{-1}$)
$\varphi_1, \varphi_2, \varphi_3,$ $\varphi_4, \varphi_5, \varphi_6$	coefficients in Eq. (2)
χ	ratio between the net water flux through the membrane and the water produced by the electrochemical reaction, dimensionless
χ_{ip}, χ_{iv}	non-ideality coefficients, dimensionless
$\psi_1, \psi_2,$ ψ_3, ψ_4	coefficients in Eq. (27), dimensionless
Ω	electrical resistance (Ωm^2)
ω	adimensional resistance
<i>Subscripts</i>	
A	referring to the SO_3^- groups in the Nafion [®] membrane
H	hydrogen
old	old value
W	water
Wt	total water
0	anodic side
1	cathodic side
<i>Superscript</i>	
*	reference condition (i.e. complete hydration)

reactant gases are usually humidified by being bubbled through high-temperature water columns before being fed into the cell. Flooding and dehydration of the membrane are phenomena to be avoided: when the first situation occurs the pores of the electrodes and the bipolar plates can be obstructed by water and will not be accessible to the gases; in the second case the membrane conductivity decreases to zero and also the damages of the membrane can occur.

The literature on PEMFC modelling includes studies on the local electrochemical kinetics of the membrane–electrode assembly [8–12] based on the analysis of mass and ion transfer. However the application of these approaches [13] involves long calculation times for only a point in the I – V cell characteristic curve.

In order to set up a tool for the dynamic prediction of cell behaviour and avoid the problems involved in other approaches, a novel approach to the problem is presented in this paper.

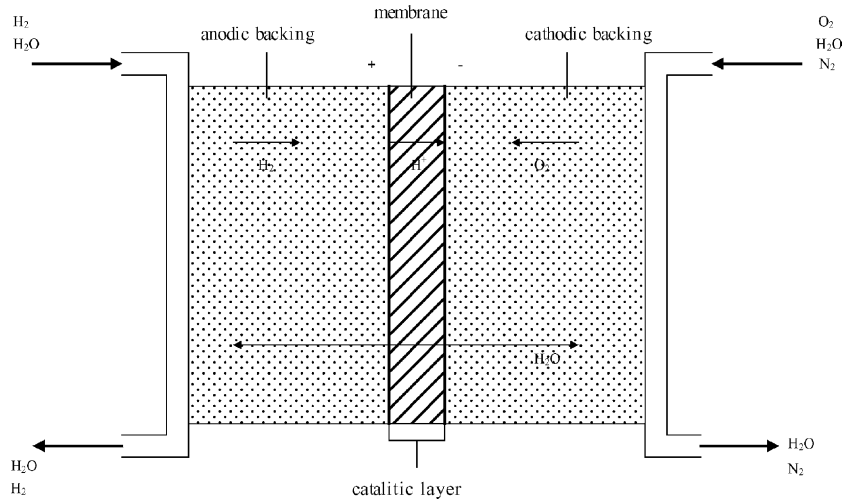


Fig. 1. Schematisation of a PEM single cell.

2. Mass and charge fluxes in conductive polymeric membrane

In a PEM fuel cell, proton conduction through the membrane is substantially due to the transport of protons in the solid electrolyte. The most used polymer for this application is Nafion[®], which has the chemical structure shown in Fig. 2.

The most important properties of Nafion[®] for ionic conduction in PEMs are:

- the presence of negatively charged sites;
- the ability to be hydrated;
- the ability to transport protons between the charged sites with a “jump” mechanism, thanks to the presence of water.

A great number of works [9,12–17] have experimentally underlined that the membrane conducts only when hydrated. The hydration originates in the humidity of the reagents and in water produced by the cathodic reaction. Indeed, some phenomena establish a water concentration gradient in the membrane.

The ion transfer phenomenon can substantially be described together with other phenomena, such as:

- Electro-osmotic water transport from the anodic side to the cathodic one (due to water “dragging” by the hydrated protons that are transferred from the anodic side, where

they are formed, to that cathodic one where they will meet the oxygen and react).

- Water diffusion, that moves from the cathode side, where the water is produced, to the anodic one where a small concentration occurs. Hydrogen ions are involved in a counter-diffusion mechanism (from the anode to the cathode).
- Pressure-driving transfer, which happens when a pressure difference is created between the anodic and the cathodic zones.

As can be seen in Fig. 1 the ionic conduction of the membrane can be described by the attributes of the charged species and of the water. Table 1 underlines the species name, its charge and mobility expressed in terms of diffusivity.

According to the semi-empirical approach of Springer et al. [17], extended by Costamagna [13], the membrane overall mass balance assumes the following expression:

$$\chi \frac{I}{n_e F} = \zeta \lambda \frac{I}{n_e F} - \frac{\rho}{M} D_\lambda \frac{\partial \lambda}{\partial x} - k \lambda \frac{\rho}{M} D_\lambda \frac{3\pi\theta}{k_b T} \frac{P_1 - P_0}{m} \quad (1)$$

The term on the left-hand side of Eq. (1) represents the total water flux through the membrane; the terms on the right-hand side are respectively the electro-osmotic drag, the water diffusion and the pressure gradient driven flow for the water in the pores of the membrane. The adimensional ratio between the membrane water concentration in the membrane and the charged sites (SO₃⁻), here identified as λ, is usually called “membrane hydration”.

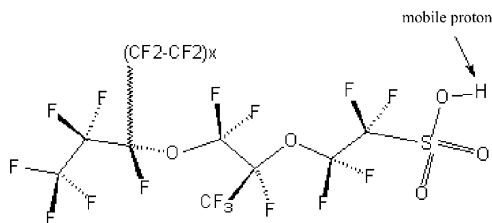


Fig. 2. The chemical structure of the Nafion[®] polymer.

Table 1
Electro-active chemical species present in the membrane

Species	Name	Charge (z)	Diffusivity
SO ₃ ⁻	A	-1	0
H ⁺ + ζ·H ₂ O	H	1	≠0
H ₂ O	W	0	≠0

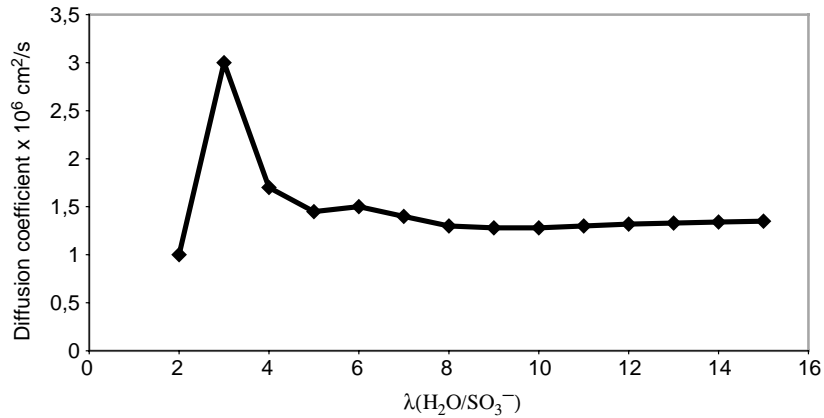


Fig. 3. Measured intradiffusion coefficient, D_λ , adapted from [17].

In equation [1], the diffusivity has been found [17] to be strongly dependent on membrane hydration:

$$D_\lambda = (\varphi_1 + \varphi_2\lambda + \varphi_3\lambda^2 + \varphi_4\lambda^3) \exp \left[\varphi_5 \left(\frac{1}{\varphi_6} - \frac{1}{T} \right) \right] \quad (2)$$

Eq. (2) represents an “equivalent” diffusivity, measured when the membrane is hydrated and, consequently, swollen by the presence of the water in its molecular structure. It does not accurately represent the diffusivity for low membrane hydration values (i.e. $\lambda < 3$), as can be seen in Fig. 3.

The membrane conductivity is evaluated in [17] as a function of the hydration along the membrane:

$$\sigma = (\gamma_1\lambda - \gamma_2) \exp \left[\gamma_3 \left(\frac{1}{\gamma_4} - \frac{1}{T} \right) \right] \quad (3)$$

So, an electrical resistance is associated to the membrane that causes a membrane voltage loss, which assumes the general expression of:

$$\eta = \Omega I, \quad \Omega = \int_0^m \frac{dx}{\sigma} \quad (4)$$

Notwithstanding this simple explanation, this model assumes without explicit mention a number of simplifications. In addition the integration of Eq. (1), where the diffusivity is expressed by Eq. (2) as a function of the membrane hydration, can cause a long calculation time and some convergence problems.

In the following pages the physical explanation of Eq. (1) will be focused on in terms of the flux of the species, a robust convergence criterion will be proposed for the integration and an approximate analytical solution that requires short computing times will be pursued by introducing a number of weighted approximations.

The flux of the species, when concentration, pressure and electric potential gradients occur, can be written following the equation (see Fig. 4):

$$\underline{J}_i = -D_i \left(\nabla \cdot C_i + \chi_{ip} \frac{C_i V_i}{RT} \nabla \cdot P + z_i C_i \chi_{iv} \frac{F}{RT} \nabla \cdot V \right) \quad (5)$$

This is substantially the Nernst–Planck equation, which is assumed to hold along the membrane thickness: non-linearity effects due to the membrane structure and variable local hydration can be taken into account by means of non-constant diffusivity coefficients $D_i(\lambda)$ and correction factors χ_{ip} , χ_{iv} .

In the membrane the general law of electroneutrality can be written as:

$$\sum_i C_i z_i = 0 \quad (6)$$

By applying Eq. (5) the total mass flux and total current is written as:

$$\underline{J} = \sum_i z_i \underline{J}_i \quad (7)$$

$$\underline{I} = \underline{J} F \quad (8)$$

Considering only the gradients on the x -axis, the flows of the three species are written by applying Eq. (5)

$$J_A = 0 \quad (9)$$

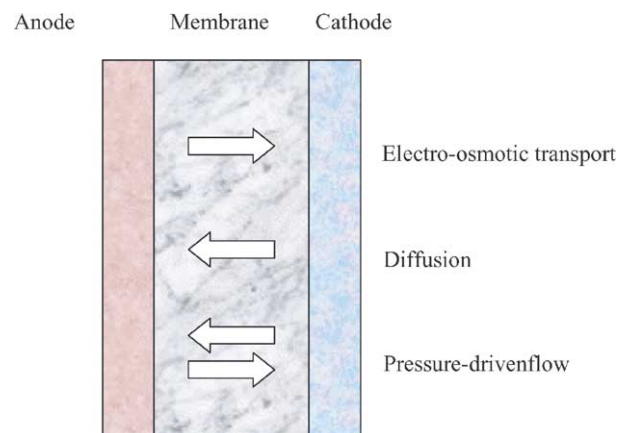


Fig. 4. Transport phenomena in the Nafion® membrane.

$$J_H = -D_H \left(\frac{dC_H}{dx} + \chi_{Hp} \frac{C_H V_H}{RT} \frac{dP}{dx} + z_H C_H \chi_{Hv} \frac{F}{RT} \frac{dV}{dx} \right) \quad (10)$$

$$J_W = -D_W \left(\frac{dC_W}{dx} + \chi_{Wp} \frac{C_W V_W}{RT} \frac{dP}{dx} \right) \quad (11)$$

$$dC_W = \frac{C_{As}}{1+e} \left(1 - \frac{\lambda}{1+e} \frac{de}{d\lambda} \right) d\lambda,$$

$$dC_H = -\frac{C_{As}}{(1+e)^2} \frac{de}{d\lambda} d\lambda \quad (19)$$

Incorporating Eqs. (10), (11), (15)–(20) in Eqs. (13) and (14) we obtain the following system:

$$J_{Wt} = \zeta \lambda J - \frac{D_W^* C_{As}}{s} \frac{D_W}{D_W^*} \left[\frac{1}{(1+e)^2} \left(1 - \frac{\lambda}{1+e} \frac{de}{d\lambda} \right) \frac{d\lambda}{dy} + \frac{V_W}{V_W^*} \chi_{Wp} \frac{\lambda}{(1+e)^2} \frac{d\pi}{dy} \right],$$

$$J = \frac{D_H}{D_W^*} \frac{D_W^* C_{As}}{s} \left[\frac{1}{(1+e)^3} \frac{de}{d\lambda} \frac{d\lambda}{dy} - \frac{\chi_{Hp}}{(1+e)^2} \frac{V_H}{V_W^*} \frac{d\pi}{dy} - \frac{\chi_{Hv}}{(1+e)^2} \frac{d\eta}{dy} \right] \quad (20)$$

The sulfonic-ion flux is zero because this ion is a part of the molecular structure of the Nafion®.

Using Eqs. (6) and (8) we have:

$$C_{AZA} + C_{HZH} = 0, \quad C_H = C_A \quad (12)$$

$$J = z_H J_H = J_H, \quad I = J_H F \quad (13)$$

According to [17], each H ion drags a number of water molecules which is approximately proportional to hydration. So, the water total flux, obtained coupling Eqs. (10) and (11), is:

$$J_{Wt} = \zeta J_H \lambda + J_W \quad (14)$$

Eqs. (9), (11) and (14) underline the fact that the transport phenomena in the membrane are sufficiently described by the total water and H-species fluxes.

In such equations electrical and pressure forces can be suitably expressed in adimensional terms

$$\eta = \frac{VF}{RT} \quad (15)$$

$$\pi = \frac{PV_W^*}{RT} \quad (16)$$

For what concerns the geometrical coordinate x , one should remember that the membrane thickness m increases when humidification occurs and it is possible to write a general swelling law dependent on the hydration as $dx/dx_s = 1 + e$, where e is a function of λ . So, it is defined a membrane coordinate system (x) and a reference one (x_s). Then, the latter can be referred to the dry thickness, so defining a dimensionless coordinate y :

$$dy = \frac{dx}{s(1+e)} \quad (17)$$

By applying Eq. (17), the concentration of the “W” and “H” components of the membrane and their dependence on hydration λ can be written in terms of swelling and dry ionic concentration C_{As} :

$$C_W = \frac{C_{As}\lambda}{1+e}, \quad C_H = \frac{C_{As}}{1+e} \quad (18)$$

Where D_W^* is the diffusivity of water in a reference condition, namely dry conditions or, better, complete hydration.

Simplifying system (20) with the relationships:

$$n = \frac{J_{Wt}s}{D_W^* C_{As}}, \quad j = \frac{Js}{D_W^* C_{As}}, \quad \gamma = -\frac{d\pi}{dy} \quad (21)$$

$$\beta = \frac{D_W}{D_W^*} \left[\frac{1}{(1+e)^2} - \frac{\lambda}{(1+e)^3} \frac{de}{d\lambda} \right],$$

$$\delta = \chi_{Wp} \frac{D_W}{D_W^*} \frac{V_W}{V_W^*} \frac{1}{(1+e)^2}, \quad \beta' = \frac{D_H}{D_W^*} \frac{1}{(1+e)^3} \frac{de}{d\lambda},$$

$$\delta' = \chi_{Hp} \frac{D_H}{D_W^*} \frac{V_H}{V_W^*} \frac{1}{(1+e)^2}, \quad \beta'' = \chi_{Hv} \frac{D_H}{D_W^*} \frac{1}{(1+e)^2} \quad (22)$$

where Eq. (21) define terms which are constant when y and λ vary, while Eq. (22) define terms which are functions of λ .

Inserting Eqs. (21) and (22) into Eq. (20) and rearranging, the system is written as:

$$\frac{d\lambda}{dy} = \frac{1}{\beta} (\zeta j \lambda - \gamma \delta \lambda - n), \quad \frac{d\lambda}{dy} = \frac{1}{\beta'} \left(j - \gamma \delta' + \beta'' \frac{d\eta}{dy} \right) \quad (23)$$

The first equation of system (23) is equivalent to Eq. (1) and their terms can be explained in the same way as those in Eq. (1). So, β is essentially an adimensional diffusivity coefficient, where the effects of the term in brackets of the first of Eq. (22) is expected to be much less important than the dependence of D_W on λ . In other words, the first of Eq. (22) puts into evidence to what extent the effective membrane diffusivity depends also on swelling; empirical expression such as Eq. (2) can obviously show only global dependence on hydration.

It is also worth noting that the dependence on λ of parameters such as β and β' is also linked to the expression chosen for the diffusive fluxes, that is Eqs. (5), (10), (11) or in terms of molar fractions, such as $J_i = -D_i C_T dy_i/dx$.

On the other hand, for what concerns the second of Eq. (23), it is apparently rather different from the empirical form (3). Obviously these differences cannot be dramatic in

practice, but they underline the necessity of a coherent formulation of water and proton transport phenomena in front of a more empirical description. A simplified and direct path is to consider that the largely most important force in determining ion flux is the electric one: in fact, of the three terms in the right hand of Eq. (10) the third is normally one order of magnitude higher than the others. So it can be assumed as:

$$\beta' \cong \delta' \cong 0, \quad j \cong -\beta'' \frac{d\eta}{d\lambda} \quad (24)$$

and β'' corresponds to the membrane conductivity of Eq. (3).

Eq. (23), reorganised in their full extension, can be written as

$$dy = \frac{\beta}{\zeta j \lambda - \gamma \delta \lambda - n} d\lambda, \\ d\eta = \left[\frac{\beta'}{\beta''} - \frac{\beta(j - \delta' \gamma)}{\beta''(\zeta j \lambda - \gamma \delta \lambda - n)} \right] d\lambda \quad (25)$$

and then integrate along the membrane thickness, from $y = 0$ to 1:

$$1 = \int_{\lambda_0}^{\lambda_1} \frac{\beta}{\zeta j \lambda - \gamma \delta \lambda - n} d\lambda, \\ \eta_1 - \eta_0 = \int_{\lambda_0}^{\lambda_1} \left[\frac{\beta'}{\beta''} - \frac{\beta(j - \delta' \gamma)}{\beta''(\zeta j \lambda - \gamma \delta \lambda - n)} \right] d\lambda \quad (26)$$

The evaluation of the membrane voltage loss can proceed by calculating a first attempted value of “ n ”, here called n_v , by considering the differential written in Eq. (23) as replaceable with the finite difference between the extreme values of the hydration of the membrane, which are a function of the external relative humidity:

$$y = 0; \lambda = \lambda_0; \eta = \eta_0, \quad y = 1; \lambda = \lambda_1; \eta = \eta_1, \\ \lambda = \psi_1 + \psi_2 a + \psi_3 a^2 + \psi_4 a^3 \quad (27)$$

Then, by adopting a Newton method for convergence, the next value of “ n ” is:

$$n = n_{\text{old}} + \frac{1 - \int_{\lambda_0}^{\lambda_1} (\beta / (\zeta j \lambda - \gamma \delta \lambda - n_{\text{old}})) d\lambda}{\int_{\lambda_0}^{\lambda_1} (\beta / (\zeta j \lambda - \gamma \delta \lambda - n_{\text{old}})^2) d\lambda} \quad (28)$$

Proceeding in this way the calculation can converge without problems. When the water flux n is known the voltage losses can be easily obtained by the second definite integration in Eq. (26).

It is possible to analyse two limit cases: if the membrane is uniformly damped the coefficients can be considered constant (at uniform temperature); in the case of the membrane being completely dry, the flow of water tends to zero, and it can be concluded that membrane resistivity is very high, according to the typical behaviour of Nafion[®] membranes and their total inability to conduct current (or protons) when not humidified.

Usually, as the membrane is not uniformly nor completely damped, the diffusivity is function of λ . Experimental evidence can be organised in terms of effective diffusivity coefficients, as in Eq. (2). So, the problem of calculating the integrals in Eq. (26) in a number of real cases can be overcome by considering the equivalence of their coefficients with that of the Springer model and adopting some approximations. Any improvement in knowledge on the behaviour of coefficients as functions of humidity and temperature can be easily incorporated in Eq. (26). On the other hand, for an approximate calculation the simplifications adopted by De Francesco and Arato [5] can be assumed. In fact, considering that the diffusion coefficient of Eq. (2) has been evaluated by fitting experimental values, it is often possible to adopt a suitable mean value.

For instance, if the first of Eq. (22), which defines the dimensionless diffusivity of water, is considered and a linear dependence $e = (\text{const. } \lambda) \ll 1$ of swelling on hydration is assumed as first approximation, we have

$$\frac{D_\lambda}{D_W} = \left[\frac{1}{1+e} - \lambda \frac{de/d\lambda}{(1+e)^2} \right] \cong \frac{1}{1+e^2} \cong 1 - 2e \quad (29)$$

and a constant mean value for β can be assumed within the limits in which a constant mean value for D_λ is acceptable [5]. Similarly constant mean values can be used for the coefficients δ , ζ .

Thanks to this approximation, the first of Eq. (25) can be integrated with a straightforward analytical path, obtaining

$$n = \alpha \left[\lambda_0 + \frac{\lambda_0 - \lambda_1}{\exp(\alpha/\beta) - 1} \right], \quad \alpha = \zeta j - \delta \gamma \quad (30)$$

This approach allows the determination of the water flux through the membrane with a very fast calculation and with results comparable to those obtained without any simplification [5]. The integration gives also, if of interest, the humidity field along the membrane thickness:

$$\lambda = \lambda_0 + (\lambda_1 - \lambda_0) \frac{\exp(\alpha y/\beta) - 1}{\exp(\alpha/\beta) - 1} \quad (31)$$

The membrane resistance can be then obtained from the integration of the second of Eq. (25); for an approximate evaluation, instead of Eq. (25), reference can be made to the position (24) and, moreover, the membrane conductivity can be expressed as a linear function of λ in a similar way as Eq. (3)

$$\beta'' = \gamma'_1 \lambda - \gamma'_2 \quad (32)$$

Remembering Eq. (31) and integrating the membrane resistance will be

$$\omega = \frac{\eta_0 - \eta}{j} = \frac{\alpha + \beta \ln((\gamma_1 \lambda_1 - \gamma_2)/(\gamma_1 \lambda_0 - \gamma_2))}{\gamma_1 n - \gamma_2 \alpha} \quad (33)$$

where α and n are given by Eq. (30).

3. Fuel cell local model

A local kinetic model of membrane and adjacent gas phases has been elaborated by using the approach presented above. Starting from the Nernst potential, the cell voltage is expressed by applying the usual definitions of the voltage losses as reported in the literature [5] and by applying the model explained here for the membrane voltage losses. In the model the water transport effects outside the membrane are neglected.

As a first application, assuming that a local model is sufficient to describe a little PEM laboratory single cell, the characteristic curves of such a cell are evaluated for average cell temperature $T = 343$ K and gas humidification $a = 0.99$. The results are compared with experimental data obtained under the same conditions [5,12] in Fig. 5.

As usual, the current–voltage curves can be schematised in three different regions: (i) semi-exponential, where the cell works in/with activation losses at the cathode at very low current density; (ii) linear behaviour, determined substantially by ohmic losses; (iii) voltage drop at high current density, due to mass transport limitations in the membrane. The model shows a good agreement that provides a validation of the membrane model and of the deduced kinetic model: in fact, by comparing these results with those reported in the literature for the non-analytical model, the main numeric differences are less than 5%, a value that can be compared with the experimental errors and does not influence the good behaviour of this approach. In addition, the calculation times are dramatically reduced from some minutes to a few seconds. So, this approach provides a new opportunity to build dynamic models of stacks containing the calculation time.

In addition, the possibility of having good results without spending excessive time in calculations will allow the imple-

mentation of this local model in direct methanol fuel cells (DMFC), by simply considering the following phenomena:

- the crossover of the methanol in the membrane [18];
- the presence of methanol in the calculation of activation and concentration voltage losses [18].

4. Conclusions

At the moment PEM fuel cells offer a very promising technology for distributed and automotive power generation. High efficiency and reduced environmental impact are the most important features of this technology.

Model analysis is very important for the design and simulation of a power generator and the approaches utilised are still affected by mathematical complexity that limits their use in dynamic simulations.

The possibility of overcoming the time-analysis problem has been studied in this work. In fact it has been shown that one of the most difficult aspects of PEM fuel cell modelisation, i.e. membrane conductivity, can be solved in an analytical way that will allow us to simulate the cell kinetic in a very short calculation time, obtaining a good agreement with experimental data.

The kinetic model presented here can be used as a basis for the future development of fuel cell mathematical approaches and, above all, in the prediction of dynamic behaviour.

The results obtained demonstrated that by considering a constant diffusion coefficient for the hydrogen ions the behaviour of the cell is correctly represented. This result will allow for further development: the implementation of the swelling experimental data and their application to a wide range of uses and direct methanol fuel cells (DMFC) by considering some particular phenomena that are influenced by the presence of methanol on the anodic site.

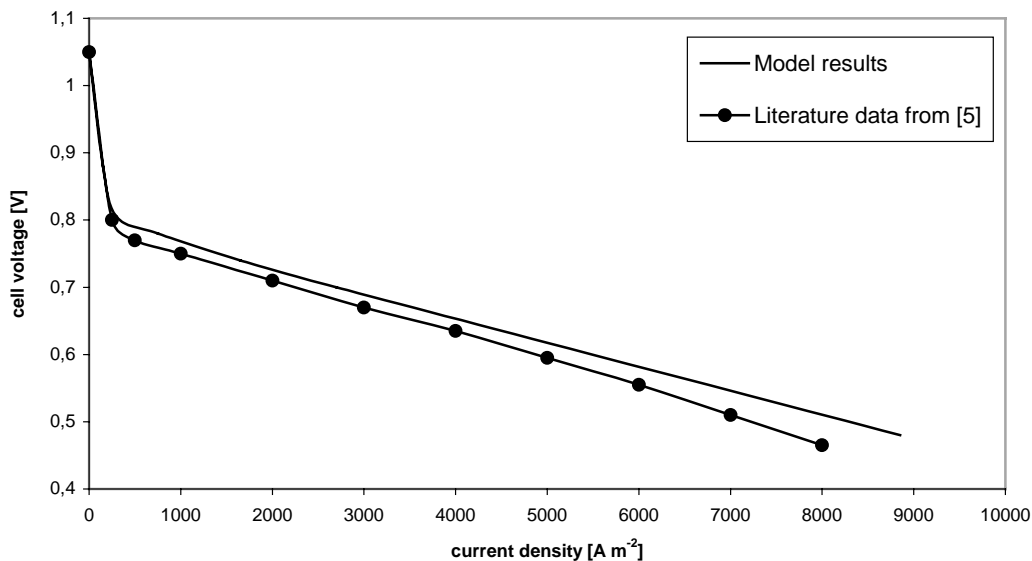


Fig. 5. Comparison between model results and literature experimental data.

Acknowledgements

This work is partially supported by Italian Department of Education, University and Research (MIUR) and Italian National Agency for New Technologies, Energy and Environment (ENEA) in the framework of financed research projects named PRIN 2001 and FISIR 2003, respectively.

References

- [1] S. Srinivasan, R. Mosdale, P. Stevens, C. Yang, Fuel cells: reaching the era of clean and efficient power generation in the twenty-first century, *Ann. Rev. Energy Environ.* 24 (1999) 281–328.
- [2] E. Arato, P. Costamagna, B. Marcenaro, Control strategies of a full size hybrid bus with second generation fuel cells, in: *Proceedings of the Second International Conference on Control and Diagnostics in Automotive Applications*, October 1998, Genoa (I), pp. 135–144.
- [3] G.H. Cole, SAE Technical Paper Series No. 891664, Society of Automotive Engineers, 1989.
- [4] M. De Francesco, E. Arato, Control strategies of the air flow rate in a PEM fuel cell hybrid bus, in: *Proceedings of the Third International Conference on Control Diagnostic in Automotive Applications CDAUTO01*, July 2001, Sestri Levante (I).
- [5] M. De Francesco, E. Arato, Start-up analysis for automotive PEM fuel cell systems, *J. Power Sour.* 108 (2002) 41–53.
- [6] J.H. Hirschenhofer, D. Stauffer, R.R. Engleman, *Fuel Cell: A Handbook (Revision 3)*, DOE/METC-94/1006 (DE94004072), US Department of Fossil Energy, Morgantown Energy Technology Center, Morgantown, WV, 1994.
- [7] J.C. Amphlett, R.F. Mann, B.A. Peppley, P.R. Roberge, A. Rodrigues, A model predicting transient responses of proton exchange membrane fuel cells, *J. Power Sour.* 61 (1996) 183–188.
- [8] J.H. Lee, T.R. Lalk, A.J. Appleby, Modeling electrochemical performance in large scale proton exchange membrane fuel cell stacks, *J. Power Sour.* 70 (1998) 258–268.
- [9] D. Thirumalai, R.E. White, Mathematical modeling of proton exchange membrane fuel cell stacks, *J. Electrochem. Soc.* 144 (5) (1997) 1717–1723.
- [10] J.C. Amphlett, R.F. Mann, B.A. Peppley, P.R. Roberge, A. Rodrigues, J.P. Salvador, Simulation of a 250 kW diesel fuel processor/PEM fuel cell system, *J. Power Sour.* 71 (1998) 179–184.
- [11] J.C. Amphlett, R.M. Baumert, R.F. Mann, B.A. Peppley, P.R. Roberge, A. Rodrigues, Parametric modelling of the performance of a 5 kW proton exchange membrane fuel cell stack, *J. Power Sour.* 49 (1994) 349–356.
- [12] Y.W. Rho, S. Srinivasan, Y.T. Kho, Mass transport phenomena in proton exchange membrane fuel cells using O₂/He, O₂/Air and O₂/N₂ mixtures. II. Theoretical analysis, *J. Electrochem. Soc.* 141 (1994) 2089–2096.
- [13] P. Costamagna, Transport phenomena in polymeric membrane fuel cells, *Chem. Eng. Sci.* 56 (2) (2001) 323–332.
- [14] D.M. Bernardi, M.W. Werbrugge, Mathematical model of a gas diffusion electrode bonded to a polymer electrolyte, *AIChE J.* 37 (1991) 1151–1159.
- [15] T.E. Springer, M.S. Wilson, S. Gottsfeld, Modeling and experimentation diagnostics in polymer electrolyte fuel cells, *J. Electrochem. Soc.* 140 (1993) 3513–3526.
- [16] E.B. Anderson, E.J. Taylor, G. Wilemski, A. Gelb, High performance hydrogen/chlorine fuel cell for space power applications, in: *Proceedings of the Fourth Space Electrochemical Research and Technology Conference*, Cleveland, OH, USA, *J. Power Sour.* 47 (1994) 3.
- [17] T.E. Springer, T.A. Zawodzinski, S. Gottsfeld, Polymer electrolyte fuel cell model, *J. Electrochem. Soc.* 138 (8) (1991) 2334–2342.
- [18] J. Cruickshank, K. Scott, The degree and effect of methanol crossover in the direct methanol fuel cell, *J. Power Sour.* 70 (1998) 40–47.