

Experimental and computational study of proton and methanol permeabilities through composite membranes

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Abstract

To design direct methanol fuel cells, proton permeability and methanol crossover have to be evaluated. A study of the transport of methanol and protons through composite membranes of poly(ethylene glycol) (PEG) and polysulfone (PSf) was performed and permeabilities of these components were determined. PSf was treated with dilute sulfuric acid to enhance hydrophilicity. PEG was found to be a good material for the active layer, because it contains —OH hydrophilic groups which combine with hydrated protons. A composite membrane made of 15 wt.% PSf and 40–50 wt.% PEG showed a lower methanol crossover ($1.0\text{E}-06\text{ cm}^2\text{ s}^{-1}$) than the commercial reference NAFION® 117. Maximal proton conductivity is also lower than NAFION® 117. A mathematical deterministic model, considering transport by diffusion through the composite membrane and equilibrium at the membrane–reservoir interfaces, was derived. However, the PEG layer did not present any pores and diffusion in the dense membrane was estimated using a transport probability. On the other hand, the porous PSf layer required an effective diffusivity that is a function of physical properties such as porosity and tortuosity. The contribution made by each mass transfer phenomenon to the total permeation was calculated by an association of mass transfer resistances.

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1. Introduction

Fuel cells, composed of an anode, a membrane and a cathode, can be used to generate energy by oxidation of either hydrogen or methanol. To take maximum advantage of the fuel, a membrane is needed to conduct protons and avoid methanol crossover.

The most representative kinds of fuel cells are the proton-exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC), which use proton-conducting membranes [1]. DMFC is more interesting than PEMFC, because its theoretical potential is higher [2], and because it allows simple liquid handling. Also, as PEMFC operation is based on the supply of hydrogen, the management of water generated is very important. This is not an issue with

DMFC, which already has a liquid phase. On the porous anode, electrochemical oxidation of the methanol occurs to produce carbon dioxide, protons and electrons. The protons diffuse through the membrane to the cathode side, where they react with the oxygen to produce water.

The most used membranes for DMFC are the perfluorinated sulfonated NAFION® membranes of DuPont, due to their chemical stability, high conductivity and high permeability to protons. However, these membranes also allow methanol to permeate, which reduces the efficiency of the electrochemical process, increases fuel consumption and damages the own cells. This phenomenon is known as *methanol crossover*. Several authors have reported the factors behind it, including cell temperature, cathode pressure, methanol concentration and catalyst morphology [3,4].

Many alternative membranes for DMFC are under investigation in the following four aspects: the primary structure of the polymer, the morphology of the polymer, the nature of the

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Nomenclature

A	membrane area (cm^2)
C	concentration (gmol cm^{-3})
d	pore diameter (cm)
D	diffusivity ($\text{cm}^2 \text{s}^{-1}$)
e	elementary charge
k_B	Boltzmann's constant
k_j	mass transfer coefficient on the membrane–reservoir j interface (cm s^{-1})
L	membrane thickness (cm)
p	number of pores of different diameters
P	permeability (cm min^{-1})
Q	volumetric permeate flow ($\text{cm}^3 \text{min}^{-1}$)
S	selectivity for proton transport
t	time (s)
T	temperature (K)
V_j	volume of reservoir j (cm^3)
x	axial position (cm)
z	non-dimensional axial position (cm cm^{-1})
Z	total ionic strength (ion m^{-3})

Greek symbols

α_j	mass transfer at reservoir j –membrane interface
ε	porosity
θ	non-dimensional time
μ	time factor
π_j	mass transfer number at reservoir j –membrane interface
τ^2	tortuosity
φ	non-dimensional concentration
Ψ	transport probability on dense layer

Subscripts

0	initial, for concentrations, or infinite dilution diffusion coefficient
c	calculated through simulations
D	diffusive
e	experimental
f	feed
H^+	proton
L	liquid
MeOH	methanol
PEG	poly(ethylene glycol) layer
PSf	polysulfone layer
s	stripping

acid group, and the nature of the medium within the polymer matrix [5]. Other membranes have been tested and results of these tests have been compared to those with NAFION® [6–8]. A better ratio between conductivity and methanol permeability has been reported. Much attention is given to polysulfone (PSf), poly(ether ketones) and poly(benzimidazole).

PSf is the simplest of these polymers and the morphologies of its membranes have been well characterized. Sulfonation is an efficient way to activate polysulfone in proton permeability. There are two methods for obtaining proton-selective PSf membranes: one is to introduce anionic moieties into a performed solid membrane [9]. The other is to introduce anionic moieties into a polymer as a kind of modification, then to dissolve of the polymer and cast it into a film [10]. The second method is more complicated from an industrial point of view, and the sulfonated polysulfone itself cannot perform as a membrane with enough physical strength. The first method is industrially easier. The treatment is with sulfuric acid, and this does not change the physical strength of a performed polysulfone membrane.

To reduce the methanol crossover, the dense layer may serve as a barrier for methanol, and at the same time may facilitate the proton transport. PEG is a kind of polymer that is widely used in many fields. For example, it is used as a lubricant and as a preservative for conserving archaeological materials, because it is reasonably inexpensive and compatible with many organic materials. In biosensors, PEG is presented as “hydrogel” [11] to immobilize enzyme or protein on the carbon electrode surface and transport electrons. PEG is therefore used as a proton-selective layer.

For the reasons outlined above, the asymmetric PSf membrane was chosen as support and treated by thermal sulfonation to improve its proton conductivity. A PEG dense layer was then produced on top of PSf support.

Despite the interest in DMFCs, only a little effort is being made to propose mathematical modelling comprising the mass transfer mechanism through the membrane [6,12]. Most studies apply an empirical adjustment to the membrane and predict the electrochemical potential generated. Traditionally, diffusivities through membranes are determined without taking into account mass transfer coefficients at the membrane–reservoir interfaces. In the case of composite membranes, a global coefficient is calculated, and the different layers are not mathematically treated separately.

We have measured the permeability of protons and methanol in membranes comprising a dense layer of poly(ethylene glycol) (PEG) and a porous layer of polysulfone (PSf). The equilibrium cell comprised a feed reservoir, the composite membrane, and a stripping reservoir. Our results are expressed in terms of diffusivity. We fed our data to a mathematical model that considered transport by diffusion through the membrane and equilibrium at the feed–membrane and membrane–stripping interfaces. We then determined diffusivity for each layer was then determined using mass transfer resistances.

2. Methods

The system used in this study comprised a feed reservoir, a composite membrane and a stripping reservoir. The PEG layer of the composite membrane faced the feed reser-

voir, and the PSf layer faced the stripping reservoir. A solution of known pH or methanol concentration is fed into the feed reservoir and the protons or methanol molecules permeate through the membrane, reaching the stripping reservoir, where the concentration is measured. It is possible then to calculate permeability for the components studied. To study permeability with this equilibrium-diffusion model, we need to:

- prepare the membrane and collect the experimental data,
- determine the experimental diffusivity,
- determine the proton, methanol and membrane properties, such as the molar volume of each component, and the porosity and tortuosity of the membrane,
- determine the proton and methanol diffusivities by correlations with the literature,
- develop an equilibrium model, to obtain transient data on concentration for each reservoir,
- associate mass transfer resistances, to evaluate the effect of each transport coefficient on experimental diffusivity, and
- calculate the selectivity of proton transport at the membrane–reservoirs interfaces and through the membrane.

2.1. Preparation of the membranes and experimental data

A polysulfone casting solution was prepared by dissolving 15 wt.% PSf (MW: 16,000, Aldrich) in *N,N*-dimethylformamide (DMF) with vigorous agitation for 12 h at room temperature. The solutions were cast onto a glass plate using a 200 μm thick casting knife, then precipitated in 15 wt.% DMF solution and/or water. The PSf membranes were then taken from the bath and rinsed with distilled water. The PSf membranes obtained were kept at 80 °C in 0.25 M H_2SO_4 aqueous solution for 3, 24 and 72 h. Excess acid on the surface was removed by a short rinse of water. The membranes were then placed in an oven at 80 °C for 1 h. These thermally treated membranes were then soaked in distilled water and rinsed daily until the pH of the rinsed water was neutral.

Usually sulfonation process requires using strong acids. However, in the present work the degree of sulfonation is not under investigation. The treatment of the PSf with dilute sulfuric acid aims enhancing proton permeability by increasing hydrophilicity of the membrane. Indeed, preliminary experiments using blank PSf membranes (not treated with H_2SO_4) provided a proton diffusivity of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$. On the other hand, after sulfonation, proton diffusivity increased to $10^{-11} \text{ cm}^2 \text{ s}^{-1}$.

Wax-like PEG (MW 1000, from Aldrich) was dissolved in methanol at several concentrations (5, 10, 20, 30, 40, 50, 60, 70 and 80 wt.%). The solution was deposited onto the top surface of support PSf membranes. The PEG-covered PSf membranes were placed in an oven to cross-link at 80 °C

for 30 and 60 min, and the composite membranes were then stored in water before use. For biosensors, often PEG film is dried overnight at room temperature to cross-link [13]. In the case studied here the PEG film was dried at 80 °C to avoid the membrane to peel off in DMF solutions.

Experiments to evaluate proton and methanol permeability were carried out by using a testing cell, consisting of two reservoirs separated by a composite membrane with a dense layer of poly(ethylene glycol) and a porous layer of polysulfone. The transversal area of tested membranes was 8.51 cm^2 and both reservoirs (that of the feed solution and that of the stripping solution) had a volume of 200 cm^3 . To measure proton permeability the feed reservoir was filled with a solution of HCl 1.0 M. Also, to evaluate methanol crossover a 1.0 M solution of methanol was used. Experimental data were the initial feed concentration C_f (methanol concentration, in M, or pH) and the initial stripping concentration C_0 . The stripping concentration was also plotted against time.

The permeability coefficient P (cm min^{-1}) was calculated according to Eq. (1):

$$-\ln \frac{C_f}{C_0} = \frac{QP}{V_f} t \quad (1)$$

Permeability was then multiplied to membrane thickness (95 μm) to obtain diffusivity ($\text{cm}^2 \text{ s}^{-1}$). Proton conductivity was obtained by using the Nernst–Einstein equation [14] as follows:

$$\sigma = \frac{DZe^2}{k_B T} \quad (2)$$

2.2. Determination of porosity and tortuosity

Important properties in mass transfer through porous media are porosity and tortuosity. In the case of tortuosity, diffusion is more difficult when the pore geometry is irregular. The diffusion mechanisms for transient and steady states are different. In the transient state, the component tends to distribute itself homogeneously for the whole solid matrix, even reaching pores that are blocked at any of the extremities. Once the system reaches steady state, there is preferential diffusion through the sections with a concentration gradient, which is the driving force for diffusion. Therefore, transport does not occur in blocked pores. To make calculations easier, we decided to determine tortuosity for the steady state, by a model that considers a porous medium as an association of pores of different diameters [15]. If we consider pores to be spheres, steady-state tortuosity may be written as in Eq. (3):

$$\tau^2 = \sum_{i=1}^p \frac{1}{d_i} \frac{\sum_{i=1}^p d_i^3}{(\sum_{i=1}^p d_i)^2} \quad (3)$$

After comparing effective diffusivity and binary diffusivity coefficients for various compounds, some authors [16] have reported that expression for tortuosity should be a function of the transported molecule structure, since cyclic and acyclic compounds have different preferential paths within

Membrane:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \Rightarrow \frac{\partial \varphi}{\partial \theta} = \pi_D \frac{\partial^2 \varphi}{\partial z^2}$$

$$\mu = \frac{L^2}{D} \quad \pi_D = \mu \frac{D}{L^2} = 1$$

$$\left\{ \begin{array}{l} \varphi(\theta = 0) = 0 \\ \frac{\partial \varphi}{\partial z} \Big|_{z=0} = -\pi_f (\varphi_f - \varphi_{z=0}) \\ \frac{\partial \varphi}{\partial z} \Big|_{z=1} = -\pi_s (\varphi_{z=1} - \varphi_s) \end{array} \right.$$

Change of variables:

$$\varphi = \frac{C - C_0}{C_f - C_0} \quad \theta = \frac{t}{\mu} \quad z = \frac{x}{L}$$

Feed – membrane interface:

$$\frac{d\varphi_f}{d\theta} = -\alpha_f (\varphi_f - \varphi_{z=0})$$

$$\varphi_f(\theta = 0) = 1$$

$$\pi_f = k_f \frac{L}{D} \quad \alpha_f = \mu \frac{Ak_f}{V_f}$$

Membrane - stripping interface:

$$\frac{d\varphi_s}{d\theta} = \alpha_s (\varphi_{z=1} - \varphi_s)$$

$$\varphi_s(\theta = 0) = 0$$

$$\pi_s = k_s \frac{L}{D} \quad \alpha_s = \mu \frac{Ak_s}{V_s}$$

Fig. 1. Equations for the feed–membrane–stripping equilibrium model.

the porous media. In our study, however, the size of transported molecules is small enough to assume there are no significant differences in transport.

By digitally treating data from scanning electron microscopy, the pore size distribution of the polysulfone (PSf) layer [17] can be evaluated. Then, tortuosity can be calculated by applying Eq. (3). Porosity, on the other hand, is the ratio of the total volume of pores to the volume of the membrane.

2.3. Feed–membrane–stripping equilibrium model

As a first approach, the system can be modelled just by considering the diffusive transport through the membrane, which is made up of a single polymeric layer. Fig. 1 shows the model equations, which consist of a partial differential equation, describing the change in concentration through the membrane, and an ordinary differential equation of each reservoir.

Our experimental data are the initial feed concentration and the stripping concentration varying on time. Data are collected and converted into stripping non-dimensional concentrations according to time. By comparing both stripping concentrations (simulated and experimental), it is possible to find the μ parameter, which relates the thickness of the membrane to the diffusivity.

We can reduce the complexity of the numeric system, which is made up of one partial differential equation (PDE) and two ordinary differential equations (ODEs), by applying finite differences. The decision on how many elements are necessary to do the simulations is based on calculated errors and required calculation time. For a hypothetic situation in which the volumes of the membrane and both reservoirs are equal, the equilibrium concentration should be one third of the initial concentration at the feed reservoir. Choosing 25 ODEs may be then justified, since a very accurate solution can then be provided (less than 1.5% error) in a short simulation time (less than 6 min), when the simulations are

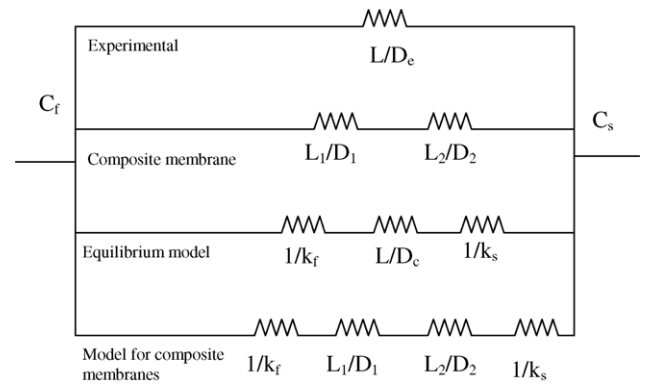


Fig. 2. Association of mass transfer resistances.

performed in a Pentium IV of 2.66 GHz with 256 MB RAM for 10,000 time iterations.

2.4. Association of mass transfer resistances

Mass transfer may be seen as a series of resistances, as in Fig. 2. Experimental diffusivity can be evaluated using a single parameter model. According to this approach, a composite membrane should have two diffusivities – one for each layer, as expressed by Eq. (4):

$$\frac{L}{D_e} = \frac{L_1}{D_1} + \frac{L_2}{D_2} \quad (4)$$

The literature reports several correlations for diffusivities and describes their relative advantages and disadvantages. To calculate diffusivities in liquids, the Wilke–Chang equation [18,19] provides acceptable data, while proton diffusivity can be determined from the Nernst–Haskell [19] equation, which is more suitable to transport of ions. To apply the Wilke–Chang equation we needed to calculate the molar volumes, which were determined according to the Le Bas rule. However, liquid diffusivity must be corrected, depending on the medium considered. For a composite membrane, one proposal is

$$D = \begin{cases} D_L \Psi \rightarrow 0 < z \leq L_{PEG}, \\ D_L \frac{\varepsilon}{\tau^2} \rightarrow L_{PEG} < z \leq L \end{cases} \quad (5)$$

When transport occurs through the poly(ethylene glycol) (PEG) layer, liquid diffusivity is multiplied to the probability of the molecule passing through the molecules. In the porous polysulfone (PSf) layer, effective diffusivity is the product of liquid diffusivity and the ratio of porosity to tortuosity. Both porosity and tortuosity, on the other hand, can be estimated by analysing the membrane with electron microscopy.

One way to find transport probability may be to assume an association of resistances for the composite membrane, as shown in Fig. 2. Using Eq. (5), experimental diffusivity can

Table 1
Equations used to determine proton selectivity

Membrane or layer	Proton selectivity
Membrane, experimental	(8) $S_e = \frac{D_{e,H^+}}{D_{e,MeOH}}$
Membrane, calculated	(9) $S_c = \frac{D_{c,H^+}}{D_{c,MeOH}}$
PEG layer	(10) $S_{PEG} = \frac{D_{L,H^+} \psi_{H^+}}{D_{L,MeOH} \psi_{MeOH}}$

be rewritten as in Eq. (6):

$$\frac{L}{D_c} = \frac{1}{D_L} \left[\frac{L_{PEG}}{\psi} + \frac{L - L_{PEG}}{\varepsilon} \tau^2 \right] \quad (6)$$

Therefore, if we accept that the solutions are dilute, we can establish a relationship between the experimental data and the simulation parameters, i.e. the transport probability and coefficients (Eq. (7)):

$$\frac{L}{D_e} = \frac{1}{k_s} + \frac{1}{k_f} + \frac{1}{D_L} \left[\frac{L_{PEG}}{\psi} + \frac{L - L_{PEG}}{\varepsilon} \tau^2 \right] \quad (7)$$

The mass transfer coefficients should be properly correlated to the chemical structure of the membrane, since they are interpreted as interaction parameters. However, for the first approach, we will assume the film mass transfer theory. According to this theory, the interfacial mass transfer coefficients are directly proportional to diffusivity and inversely proportional to boundary layer thickness [20].

2.5. Selectivity for proton transport

Once the experimental and calculated diffusivities and the mass transfer coefficients are obtained, the selectivity can be calculated for proton transport at the membrane–reservoirs interfaces and through the membrane. Table 1 lists the procedures for determining selectivities. Eqs. (8)–(10) in this table can be used to analyse each transport process separately and evaluate selectivity for different membrane compositions.

3. Results and discussion

In this section we present our experimental results and the data obtained from simulations.

3.1. Physico-chemical properties

By analysing the membrane using electron microscopy and the equations in Section 2, we determined porosity and tortuosity for the polysulfone layer. Table 2 lists the average data for the membranes, the thickness of both layers, expressed in micrometers and the diffusivities calculated from Wilke–Chang (for methanol) or from Nernst–Haskell (for protons, in this case considered as HCl molecules) theories. Although thickness of PEG layer may vary according to the PEG content in the casting solution, we assumed an average value of 1 μm for all membranes. Tortuosity shows that the

Table 2
Physico-chemical and geometric data

Property	Value
L (μm)	95.00
L_{PEG} (μm)	1.00
A (cm^2)	8.51
ε	0.13
τ^2	1.04
D_{MeOH} ($\text{cm}^2 \text{s}^{-1}$)	1.70E–05
D_{H^+} ($\text{cm}^2 \text{s}^{-1}$)	3.33E–05

membrane structure was well represented by a sequence of straight channels, because the value was not far from 1.0.

3.2. Experimental data

The membranes were placed in the equilibrium cell between the feed and the stripping reservoirs, and the concentration (for methanol crossover experiments) or pH (for proton permeability experiments) was measured. Initial feed pH in all experiments was 0.12.

We made preliminary experiments using NAFION[®] 117. Methanol crossover of $2.54\text{E}–06 \text{ cm}^2 \text{ s}^{-1}$ was obtained, in perfect agreement with values available in the literature [21]. Proton diffusivity was $9.54\text{E}–06 \text{ cm}^2 \text{ s}^{-1}$. Therefore, by using Nernst–Einstein equation, diffusivity was converted to proton conductivity (71.80 mS cm^{-1}).

Composite membranes used had a polysulfone (PSf) (15% PSf–water) porous layer covered by a PEG layer. Diffusivities are presented in the Fig. 3. Proton permeation presents a maximum for a membrane with 50 wt.% of PEG in the casting solution. On the other hand, maximal methanol crossover for composite membranes is less than a half of the value obtained using NAFION[®] 117. Data of proton conductivity (Fig. 4) of composite membranes may help assessing if they are appropriated for fuel cells. Proton conductivity for the composite membranes is still too low if compared to NAFION[®] 117.

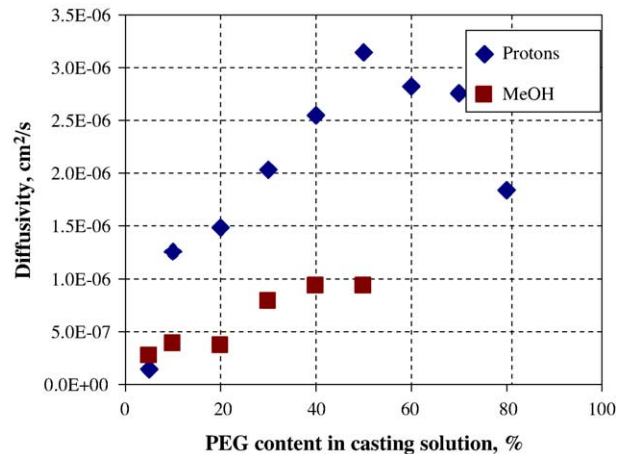


Fig. 3. Experimental diffusivities for proton and methanol.

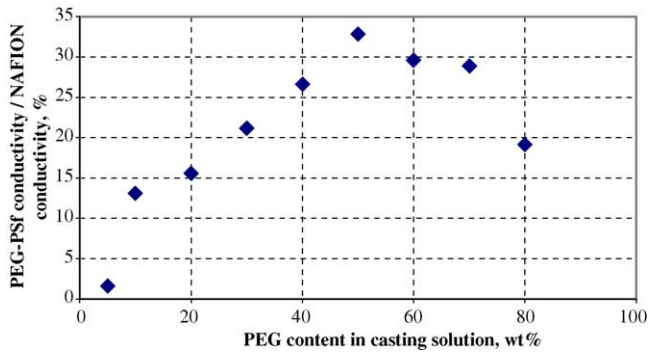


Fig. 4. Correlated proton conductivity, compared to value obtained using NAFION[®] 117 (71.8 mS cm⁻¹).

3.3. Determination of transport probability

From the association of mass transfer resistances we divided our experimental results for diffusivity into the several factors that contribute to its value. In this section, we analyse transport probability (see Fig. 5), which shows the change in the transport probability of protons and methanol through the dense layer, depending on the content of PEG in the casting solution.

We used the equilibrium model to calculate the transport probability from our experimental data. Simulations were performed in FORTRAN as follows:

1. Experimental concentrations were converted into non-dimensional concentrations varying (in terms of dimensional time), according to the equations presented in Section 2.
2. Interfacial mass transfer coefficients were set to 1 (case of low external mass transfer resistance).
3. Simulation was performed until the calculated non-dimensional concentrations (in terms of non-dimensional time) reached the maximum values of the experimental non-dimensional concentrations of the stripping solution.
4. Experimental and simulated non-dimensional concentrations were compared and the values of the calculated diffusivities were found.

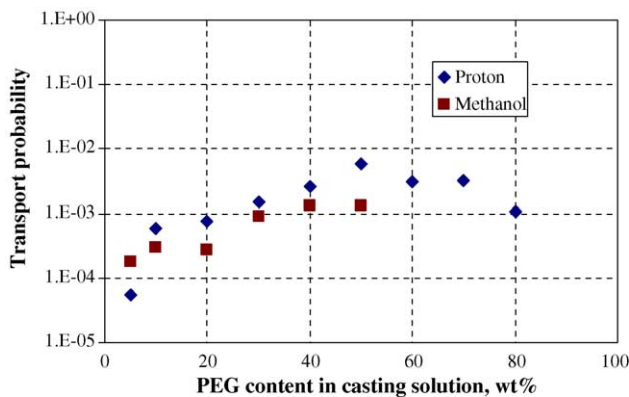


Fig. 5. Transport probabilities for protons and methanol obtained through the equilibrium model.

Table 3

Proton selectivity

w_{PEG} (wt.%)	S_e	S_c	S_{PEG}
5	0.570	0.663	0.608
10	3.210	3.289	3.877
20	4.094	4.132	5.372
30	2.542	2.554	3.227
40	2.714	2.606	3.872
50	3.349	3.232	8.807

5. The transport probabilities were calculated from the correlation between experimental and calculated diffusivities.

Fig. 5 compares the transport probabilities for protons and for methanol, determined by the equilibrium model. The PEG content in the casting solution determines the number of active sites that are responsible for the mass transfer. The transport probability for protons increased significantly when the PEG content increased from 10 to 50 wt.% and reached a maximum at this composition. Thereafter, the probability decreases, because the amount of PEG in the casting solution also helped to block any transport paths. This was because, in the dense layer, transported molecules had to pass in the free spaces between molecules. The more concentrated was the casting solution, the fewer the free spaces there were when the solvent was evaporated and the PEG layer was formed. This effect of maximum can also be seen by analysing the fit of the transport of methanol. In this case, probabilities were much lower, because:

- the molecules of methanol are much bigger than protons, so there is less space between PEG molecules is reduced for such component,
- fewer molecules of methanol are transferred by electronic effects than protons.

Transport probabilities could be estimated in a first attempt as the ratio of the molecule size to free volume in the polymer cell size. If there was a correlation between the PEG content in the casting solution and the polymer conformation, the transport probabilities of any molecule, once its molar volume had been calculated, could at least be estimated in order to design a membrane to separate one of two components or, as in the present case, to allow protons to flow and avoid methanol crossover.

As mentioned in Section 2, we can also use these results to calculate proton selectivity (see Table 3). Whether calculated directly from experimental data or indirectly by applying the equilibrium model, selectivity was maximum for a membrane with 20 wt.% of PEG in the casting solution. This property could also be calculated for the PEG layer. This was maximum for 50 wt.%, which shows that selectivity may increase if another support layer is used.

From these results, we calculated the relative resistance of each mass transfer phenomenon to the experimental diffusivity. See Fig. 6 for data on protons and Fig. 7 for data on methanol. The resistance to the permeation of pro-

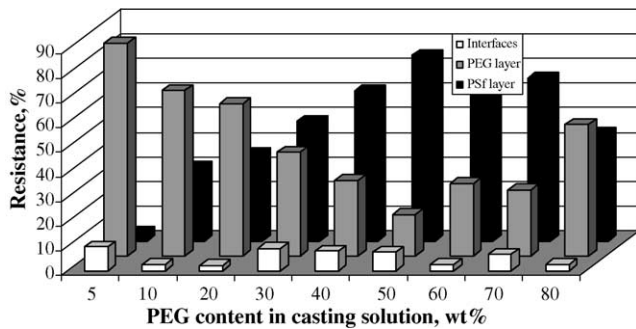


Fig. 6. Relative contribution of each mass transfer phenomenon to total resistance to permeation of protons.

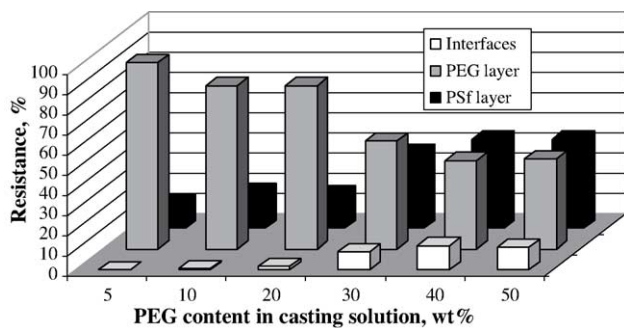


Fig. 7. Relative contribution of each mass transfer phenomenon to total resistance to permeation of methanol.

tons of the PSf layer was maximum when the PEG content in the casting solution was 50 wt.%. When we evaluated the methanol crossover, we found that the resistances of the two layers were almost equal at this composition. When membrane–reservoirs equilibrium was instantaneous, the mass transfer resistance at both interfaces could be as much as 10%, which confirms that this effect must be taken into consideration when simulating membrane permeation. It is important to evaluate mass transfer coefficients because they govern equilibrium at membrane–reservoir interfaces and also promote the transport through the membrane by increasing chemical potential. Mass transfer coefficients represent the relative affinity of the membrane for a given component and may be used to recommend optimal materials.

4. Conclusions

In this study we aim to contribute to the phenomenological knowledge of the permeation transport processes occurring in a fuel cell, by identifying the dominant mechanisms and contributions to permeability of mass transfer phenomena. The permeation of protons and methanol through composite membranes provided data for modelling. The main conclusions of this study are:

- The composite membranes tested provided a lower methanol crossover than NAFION® 117. As this happens

also for proton permeation, more materials should be tested in order to manufacture a fuel cell with better performance.

- Transport probabilities for protons and methanol were maximum for the membrane whose casting solution had 50 wt.% of PEG. For higher PEG contents, there may be less free space for transport in the dense layer, so transport probability decreased.
- Overall selectivity is maximum for a membrane with 20 wt.% of PEG in the casting solution. However, this value was higher when only the PEG layer was considered, which indicates that selectivity may be enhanced if another support layer is used.
- When evaluating the resistance of the different mass transfer phenomena, the PEG layer had the lowest resistance when the casting solution had 50 wt.% of PEG. Choosing a suitable porous support may reduce total mass transfer resistance and increase overall selectivity.
- Even if we consider instantaneous membrane–reservoirs equilibrium, the interfacial mass transfer resistance may represent 12% of the total mass transfer resistance.

At the moment, this model only takes into account the diffusive processes. However, in the values of diffusivity obtained through simulations other effects, like complexation reactions or hopping, may appear. Physico-chemical interactions of the membrane with the transported species should also be considered, for example by the Enskog–Thorne theory.

Once the transport phenomena have been evaluated, we can derive a phenomenological model for the whole fuel cell, including the kinetics of methanol oxidation. Unlike those already published, this model will not treat the membrane as a black box and will not depend exclusively on experimental data. It can therefore also recommend materials for a better fuel cell performance.

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