



New approach for the evaluation of membranes transport properties for polymer electrolyte membrane fuel cells

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ABSTRACT

The two major hurdles obstructing the large scale commercialization of PEMFCs (polymer electrolyte membrane fuel cells) are the cost and durability under a wide range of operating conditions. Among the main factors affecting the PEMFC, the durability of the polymeric membrane is one of the most determinant.

Ideally, the membrane present in the MEA should be impermeable to gases such as H₂, O₂, N₂, letting past only the H⁺ from the anode to the cathode side. However, gases permeate the membrane giving the so-called “crossover”. The crossover cannot be considered negligible specifically when the membrane thickness is lower and lower. Nevertheless, the rates of hydrogen and air/oxygen permeation to the opposite side of the membrane are relatively slow, the crossover leads to a depletion of PEMFC efficiency and accelerates the degradation of the polymeric membrane. The evaluation of the permeation of gases through the membranes usually used in the PEMFC becomes, thus, fundamental in the estimation of the overall PEMFC performance.

In this work, a new approach for the systematic evaluation of the mass transport properties of a PEM is proposed. A protocol for permeation measurements has been elaborated to compare the transport properties of different membranes as a function of the same operating conditions due to the strict dependence of the membrane performance on the relative humidity (RH) and temperature. The method has been proven on two different membranes: a Nafion 117 and a cross linked home-made SPEEK membrane.

The proton conductivity represents the other transport property of the membrane to be considered together with the gas permeation properties. The ideal/desired membrane must exhibit low gas permeability and high proton conductivity. Moving in this logic, in the present work a new parameter called *Transport Performance Index* has been defined as the ratio of hydrogen permeability and proton conductivity. This leads to an immediate idea of the whole mass transport performance of the membrane. The mass transport properties, proton conductivity and *Transport Performance Index* were measured for Nafion 117 and SPEEK membranes as a function of temperature, pressure, and relative humidity feeding different gaseous streams. The properties of the different membranes were also critically compared.

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1. Introduction

In the last few decades, a great deal of attention has been focused on the development of polymer electrolyte fuel cell (PEMFC) as primary power media for electrical vehicles and stationary applications. However, contrary to what was foreseen in the past, namely that PEMFCs would be commercialized in stationary applications by 2001 and in transport applications as early as 2003 [1], to

date only few applications have been proposed on the market and several technical challenges remain for the on-board storage and infrastructure for hydrogen fuel, as well as for the fuel cell system itself [2]. The two major hurdles obstructing the large scale commercialization of PEMFCs are the cost and durability under a wide range of operating conditions. The main factors affecting the PEMFC durability can be summarized in the catalyst layer degradation [3], gas diffusion layer degradation [4], and degradation of the polymeric membrane [2,5]. The membrane accounts for around 6% [6] to 30% [7] of the cost of a PEMFC, therefore, the study of its properties and its performances becomes quite important. The role of the membrane in the PEMFC is to separate the anode and the cathode

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electrodes acting, in the meantime as a proton conductor and an electron insulator. In theory, the amount of gases permeating through the membrane and, thus, passing from the anode to the cathode and vice versa, could be considered negligible. However, there is always some amount of gases which permeates through the membrane and that cannot be considered negligible as the membrane thickness is much lower. Since the improvement of the proton conductivity of the membranes leads to a lesser thickness, the evaluation of the permeation through the membrane becomes fundamental in the estimation of its performance. Obviously, during the PEMFC operation, the gases permeating through the membrane are hydrogen, oxygen and nitrogen, in the case when the PEMFC is fed with air. The permeation of these gases is called “crossover”.

The hydrogen and oxygen that permeate through the membrane are consumed with the generation of heat and water without the generating of useful work, leading to a low fuel and PEMFC efficiency without producing electrons, since catalytic sites are “occupied” by the not-useful reaction. Even though the rates of hydrogen and air/oxygen crossover to the opposite side of the membrane are relatively slow and result in only 1–3% loss in fuel cell efficiency, the highly exothermic reaction between H_2 and O_2 and the associated production of peroxide and hydroperoxide radicals are responsible for chemical membrane degradation which, in their turn, cause mechanical degradation and consequent failure of the membranes [2]. Furthermore, the inert nitrogen entering the cathode permeates through the membrane to the anode stream. Thus, the nitrogen content at the end of the anode flow stream increases, leading to localized fuel starvation, which can cause carbon corrosion at the cathode electrode [8]. As it clearly appears, one of the key-factors that influences the durability of PEMFC is the permeability to gases; therefore, its impact on fuel cell operation is an important parameter that needs to be characterized under different, realistic, fuel cell operating conditions for use in the development and advancement of PEMFCs. Several works, in the literature refer to the assessment of the mass transport properties of membranes [7–10,11,14], and the methods for the evaluation of these parameters are significantly different from each another. These include the volumetric method, time-lag technique, gas chromatography method, and electrochemical monitoring techniques. Some of them [8] measure the permeability coefficient of hydrogen and oxygen in Nafion® membranes using the volumetric method, where a high pressure is applied to one side of the membrane and the permeating flux of the gas is measured at the other side. The time-lag technique is another kind of volumetric method but, in this case, the time to fill up fixed downstream volumes is measured instead of the flow rate for a given sample area [8,12]. Analogously, gas chromatography methods are used by measuring concentration change downstream of the membrane when the same total pressure but different gas concentrations are applied through the membrane [11].

An alternative way to measure the gas permeability coefficient foresees the use of the electrochemical methods. In this case, the membrane is already assembled in the MEA and one of its sides is exposed to an acid solution with a counter electrode, and current is generated due to the crossover gas, while a reactive gas is supplied to the other side of the membrane and is measured over time to estimate the diffusion coefficient and solubility coefficient of the gases in the membrane [9]. Each of these methods shows advantages and drawbacks, however, up to now a standardized method for the evaluation of the mass transport properties of the membrane to be used in PEMFC has not yet been identified. The measuring of the mass transport properties and thus the crossover in conditions as close as possible to the real situation appears important; therefore, the electrochemical methods result more suitable for this type of measurement. On the otherhand, the

systematic analysis of the mass transport properties by the volumetric method allows more detailed information on the behaviour of the membrane alone to be deduced, supplying important feedback for the improvement of the membrane properties during its preparation.

As widely described in the open literature [13], the performance of an electrolyte in PEMFC applications is strictly related to the “hydrothermal history” of the membrane. This means that the behaviour of the membrane and its durability are strongly affected by the combined values of temperature and relative humidity in which they are operated. The identification of a protocol for the measurements is important to compare the mass transport properties of different membranes, so that all the membranes compared undergo the same hydrothermal history.

In this work, a new approach for the systematic evaluation of the mass transport properties of a polymer electrolyte membrane is proposed. Owing to the strict dependence of the membrane performance on the relative humidity (RH) and temperature, a protocol for permeation measurements has been elaborated to compare the transport properties of different membranes correctly as a function of the same operating conditions.

The method has been proven on two different membranes: a Nafion 117 and a cross linked home-made SPEEK membrane. Over the past 30 years, in fact, Nafion perfluorosulfonic acid (PFSA) ionomer and membranes produced by E.I. DuPont Co. have been widely used in PEMFC applications. However, these polymers are quite expensive and exhibit high permeability towards gases, leading to important crossover phenomena which provoke a reduction in the overall PEMFC efficiency. A Nafion 117 membrane (typical thickness 183 micron) was used for its higher thickness with respect to a Nafion 115 membrane (typical thickness 127 micron). Thus, the Nafion 117 membrane is expected to be more resistant than the other, being the same the other properties of the material, that is Nafion.

Sulfonated aromatic polymer (SAP) membranes could represent a suitable alternative to the PFSA membranes. These ionomers are less expensive than PFSA but, unfortunately, are also less resistant to radical attack. Their lower O_2 and H_2 permeability with respect to Nafion is not sufficient to avoid fuel crossover [14]. Furthermore, this polymer family suffers from other important limits such as high swelling and poor mechanical properties in high humidity conditions. Cross-linking of SAP membranes is a reasonable way to improve their dimensional stability and avoid swelling without significant decrease of proton conductivity [15,16]. In addition, the cross-link is expected to reduce the gases permeability.

The two membranes underwent the same testing protocol for the evaluation of the mass transport properties, which were measured opportunely tuning the temperature and the relative humidity.

Proton conductivity, the other transport property of the membrane to be considered, and gas permeation have to be taken into account to really compare the membrane performance. In fact, the ideal/desired membrane must exhibit low gas permeability and high proton conductivity. Moving in this logic, it could be useful to identify a single parameter, called *Transport Performance Index*. This, taking into account all the mass transport properties, leads to an immediate idea of the whole mass transport performance of the membrane.

In this work, the mass transport properties, proton conductivity and *Transport Performance Index* were measured for Nafion and SPEEK membranes as a function of temperature, pressure, relative humidity feeding different gaseous streams. The properties of the different membranes were also critically compared.

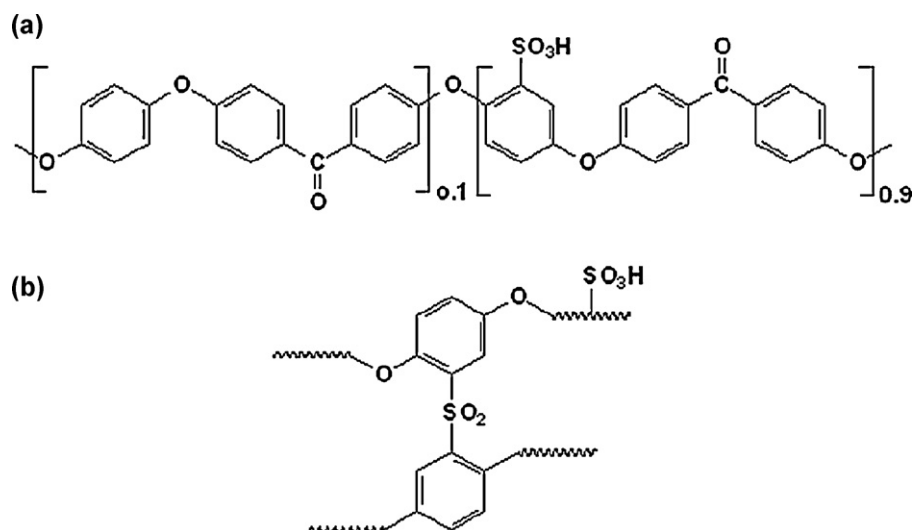


Fig. 1. Chemical formula of the SPEEK polymer with degree of sulfonation 0.9 (a); and scheme of the crosslinked polymer (b).

2. Materials and methods

2.1. Preparation of SPEEK membrane

Poly(ether ether ketone) PEEK (Victrex 450P, MW = 38,300 g mol⁻¹) was sulfonated following the procedure already reported in a previous work [17] (Fig. 1).

The degree of sulfonation, measured by ¹H NMR spectroscopy and by titration, was equal to 0.9, corresponding to an ion exchange capacity of 2.5 meq g⁻¹. The membranes were prepared by phase inversion technique, using dimethylsulfoxide (DMSO) as solvents (Sigma Aldrich) according to the procedure described in [15]. After casting the membrane underwent two thermal treatments for promoting the cross linking reaction (Table 1), which occurred leading to membranes with a final degree of sulfonation equal to 0.6. The same permeation measurements carried out on the SPEEK membrane were performed on a commercial sample of Nafion 117, for comparison.

Nafion 117 membrane was purchased from Quintech (Germany). Prior to testing, Nafion 117 membrane was pre-treated as follow: boiled 1 h in H₂O₂ 3%; boiled 1 h in H₂O; boiled 1 h in 1 M H₂SO₄; boiled 1 h in H₂O.

2.2. Proton conductivity measurements apparatus

Membranes disks, 8 mm in diameter and 90–100 μm thick for SPEEK and 180 ± 4 μm for the Nafion 117 membrane, were sandwiched between gas diffusion electrodes (Pt-free ELAT), which were pressed on the membrane faces by means of porous stainless steel discs; the applied pressure was 58.8 bar for SPEEK and 26 bar for Nafion. The through-plane membrane conductivity was determined as a function of temperature and RH by impedance spectroscopy with a Solartron SI 1260 Impedance/Gain Phase Analyser at signal amplitude ≤ 10 mV. All the conductivity values here

reported refer to measurements carried out after the conductivity had reached a constant value for at least 2 h.

RH was controlled by using a stainless steel sealed-off cell consisting of two interconnected cylindrical compartments held at different temperatures. The cold compartment contained water, whereas the hot compartment hosted the membrane electrode assembly (MEA). Relative humidity in the hot compartment was calculated from the ratio between the pressures of saturated water vapour (*p*) at the temperatures of the cold (*T*_{cold}) and the hot (*T*_{hot}) compartment:

$$\text{Relative Humidity, RH} = \frac{P_{\text{H}_2\text{O}}^{\circ}(T_{\text{cold}})}{P_{\text{H}_2\text{O}}^{\circ}(T_{\text{hot}})} \cdot 100 \quad (1)$$

2.3. Permeation experiments apparatus

The transport properties of the membranes were investigated feeding H₂, O₂ and N₂, as pure gases at different temperatures and operating trans-membrane pressure differences, in order to measure the permeating flux and evaluate the membrane properties such as permeance and permeability in conditions as much as possible close to the real applications of the membrane in MEA. For this reason any gas was fed at different values of humidity (50–100%) in a temperature range of 80–120 °C. Table 2 reports the operating conditions adopted during the experiments.

The membrane was tested in the apparatus schematized in Fig. 2.

The core of the set up is the flat sheet membrane hosted in a module. This module is a stainless steel cell with two chambers: the feed and the permeate side. The feed chamber has an entering and an exit stream (feed and retentate), whereas the permeate chamber has only an exit stream. The different membranes, supported by a porous stainless steel disc (0.2 μm pore grade), to supply the required mechanical resistance and sealed by means of rubber o-rings, were assembled in the cell. The net membrane area available for permeation was ca. 20 cm².

Table 1
Membrane characteristics and operating conditions used for the thermal annealing of the membrane.

Membrane material	SPEEK
I thermal annealing (after membrane casting)	120 °C for 24 h
II thermal annealing (after membrane casting)	180 °C for 24 h
Degree of sulfonation after cross-linking	0.6

Table 2
Operating conditions used for the permeation experiments.

Temperature, °C	80, 100, 120
RH, %	50, 75, 100
Feed pressure, bar	2–10
Permeate Pressure, bar	1
Feed gas	H ₂ , N ₂ , O ₂

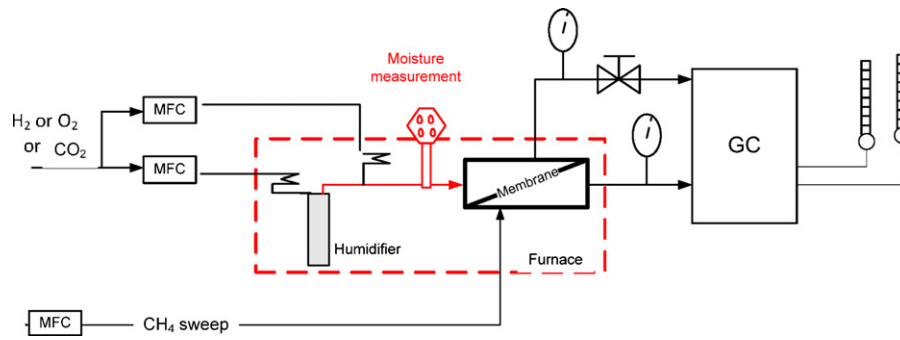


Fig. 2. Scheme of the apparatus used for permeation experiments.

The desired level of humidity was obtained mixing two streams of the same gas: the first water saturated (100% relative humidity) by feeding a dry stream to a humidifier placed at the same temperature and pressure as the membrane module and the other completely dry. Any value of the relative humidity in the feed stream was obtained weighting these two streams. The feed flow rates were controlled by means of opportunely calibrated mass flow controllers. The membrane module was fed from the bottom to avoid any water condensation on the membrane surface. Eventual water excess remained in the module chamber and did not hinder the permeation, covering the membrane surface.

The feed, permeate and retentate streams contained at least two species: the gas (e.g., H₂, O₂ or N₂) of interest and the water used for the humidification. Therefore, the permeance evaluation, also of a specific single gas was made by using the Concentration Gradient Method. A back pressure regulator on the retentate line allowed the required trans-membrane pressures difference to be operated in the cell. The retentate and permeate flow rates were measured by means of two bubble soap flow meters, after the condensation of all the water contained in the two outlet streams.

The main equations used for calculating the mass transport properties of the membrane, once the permeating flow rate, retentate and permeate pressure were measured, are reported in the following equations:

$$\text{Permeating flux}_i = \frac{\text{Permeate flow rate}_i}{\text{membrane area}} \text{ L(STP) m}^{-2} \text{ h}^{-1} \quad (2)$$

$$\text{Driving force} = \Delta P_i^{\text{TM}} = P_i^{\text{Retentate}} - P_i^{\text{Permeate}}, \text{ bar} \quad (3)$$

$$\text{Permeance}_i = \frac{\text{Permeating flux}_i}{\Delta P_i^{\text{TM}}}, \text{ L(STP) m}^{-2} \text{ h}^{-1} \text{ bar}^{-1} \quad (4)$$

$$\text{Permeability}_i = \frac{\text{Permeating flux}_i}{\Delta P_i^{\text{TM}}} \text{ thickness}^{\text{Membrane}}, \text{ L(STP) m m}^{-2} \text{ h}^{-1} \text{ bar}^{-1} \quad (5)$$

Standard temperature and pressure (STP): 0 °C; 1 bar.

Eqs. (2) and (3) report the permeating flux and the corresponding driving force for the *i*th species permeating the membrane. The permeance, the ratio of the permeating flux and driving force, the slope of the linear fitting through the axes origin of the permeating flux as a function of the corresponding driving force, can be evaluated by Eq. (4). The permeability is defined as the permeance multiplied by the membrane thickness (Eq. (5)).

In this paper, the experimental results were analyzed considering the permeance instead of the permeability. This was mainly due to taking into account the slight changes that can occur in membrane thickness in dependence on RH, temperature and trans-membrane pressure difference values. However, the permeability was used instead of permeance in the comparison of the different

membranes properties owing to the different samples thicknesses. In fact, the permeability does not depend on the membrane thickness.

2.4. Protocol for mass transport experiments

Owing to the strict dependence of the membrane performance on the RH and temperature, a protocol for permeation measurements has been elaborated to compare the transport properties of different membranes correctly as a function of these operating conditions.

The mass transport measurements (permeation tests) started feeding H₂ at 80 °C and RH = 50%. Then hydrogen was replaced by N₂ keeping the same temperature and RH. Afterwards, nitrogen was replaced by O₂, always at 80 °C and RH = 50%. An analogous sequence (H₂, N₂, O₂) was repeated once for higher RH (75%) and again for RH = 100%, at the same temperature. A total of nine steps complete this first part. The same sequences were repeated at the higher temperature values of 100 °C and 120 °C. The experiments were performed continuously and the membrane was left overnight under a gaseous stream at 2 bar. Fig. 3 shows more about the specific sequence and combination of these variables.

3. Results and discussion

3.1. Mass transport measurements

As already mentioned, the cross-over of the fuel and oxidant not only reduces the PEMFC efficiency, but, also favours the failure of the membrane because radical species produced at the electrodes can attack the polymer. The evaluation of the membrane transport properties, measured in conditions close to the ones used in real applications provides a fundamental indication about one of the aspects to take into account in the choice of an electrolyte suitable for PEMFC applications.

The permeating flux of each gas increased linearly with the corresponding permeation driving force, for all the experiments carried out and for each membrane considered; therefore, a constant permeance value was assumed for each gas, since the difference among experimental results and linear regression through the axes origin (i.e., the permeance) was lower than 2%.

Therefore, the next analysis is proposed in terms of permeance, which includes the membrane “behaviour” in the whole ΔP_i considered.

3.2. Permeation experiments on SPEEK membrane

The permeance of H₂, N₂ and O₂ has been evaluated as a function of the relative humidity, for all the three temperatures investigated. As can be seen in Fig. 4a, at 80 °C the permeance slightly decreased as the relative humidity increased. The permeation of all

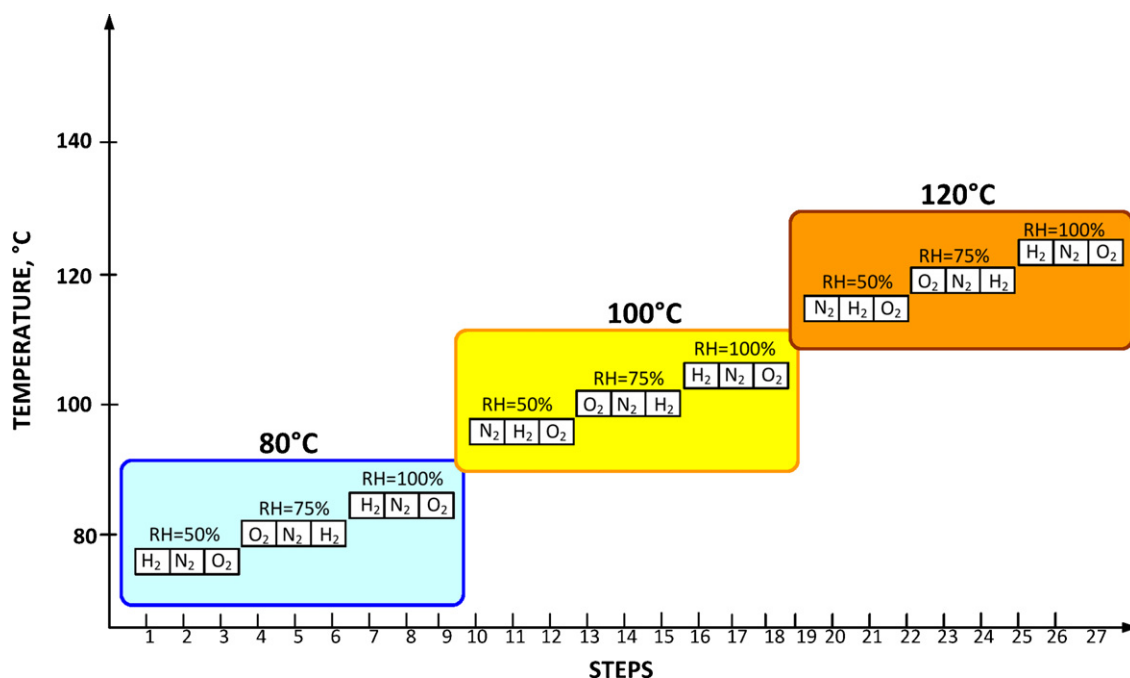


Fig. 3. Mass transport measurements – experimental procedure.

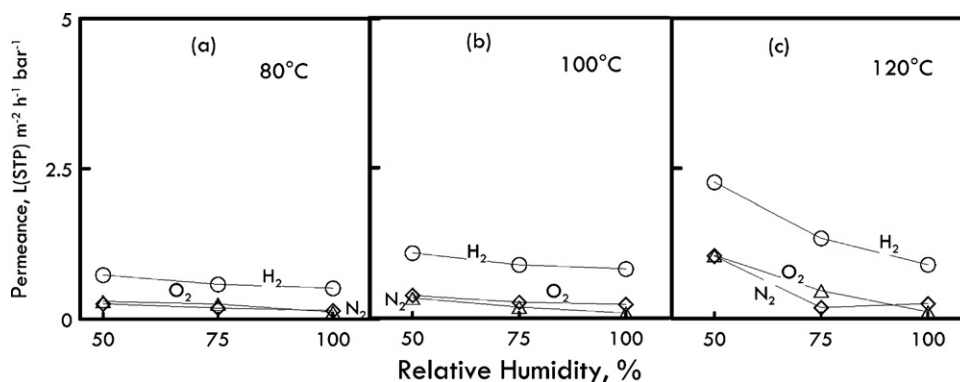


Fig. 4. SPEEK – H₂, N₂, O₂ permeance as a function of relative humidity, for (a) 80 °C, (b) 100 °C and (c) 120 °C.

the three gases through polymeric dense membranes is essentially determined by the diffusive transport mechanism. The reduction of the permeance with RH could be attributed to the water uptake increase that produces a change in the polymer matrix, creating a reduction of diffusive transport of the gas. In the whole RH range considered, H₂ permeance was higher than those of O₂ and N₂. Following the procedure indicated in the previous section, the temperature was increased to 100 °C (Fig. 4b). Also in this case the permeances of all gases slightly decreased with RH and the H₂ one was always higher than N₂ and O₂ permeances. At 120 °C, the permeance decrease corresponding to RH increase was much more evident than at the other temperatures investigated (Fig. 4c). The experimental results confirmed that the crosslinked SPEEK membrane was quite resistant, since it was able to withstand drastic changes in operating conditions. Moreover, it must be pointed out that during the permeation measurements the membranes are exposed to a high pressure, necessary for creating the driving force responsible for the permeation, therefore they undergo extra stress, which does not occur during their use in MEA.

The permeation of gaseous species through the membrane is an activated mechanism that follows the Arrhenius law. For this

reason, at each value of RH, the permeance of all the gases used in the experiments increased with the temperature (Fig. 5). However, at RH = 100% this permeance increase was less evident than at the lower RH% values (Fig. 4c).

3.3. Permeation experiments on Nafion 117

To evaluate the suitability of thermally annealed SPEEK membranes for high temperature PEMFC applications, it is important to compare their transport properties with the native Nafion 117 ones, which currently represents the most used electrolyte in PEMFC and, thus, a reference material. The transport properties of the commercial Nafion 117 were measured and compared with the results of the SPEEK, following the same procedure described in Fig. 3.

Contrarily to the permeance trend of the SPEEK membrane, at 80 °C the Nafion 117 showed quite constant values of the permeances as RH increased, for all the investigated gases (Fig. 6a). Basically, the same trend was observed at 100 °C, even if a slight decrease of H₂ and O₂ permeance was recorded (Fig. 6b). At 120 °C, the membrane started to change its behaviour, particularly for RH = 75% (Fig. 6c). As can be seen, a dramatic increase in the H₂

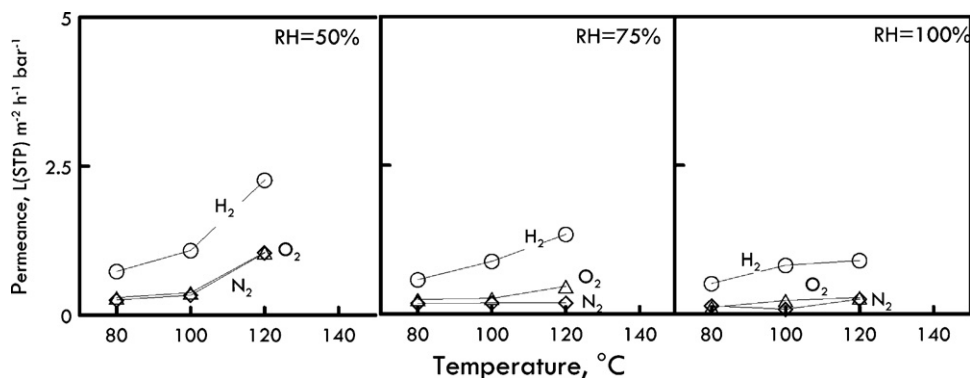


Fig. 5. SPEEK – H₂, N₂, O₂ permeance as a function of temperature, for (a) RH=50%, (b) RH=75% and (c) RH=100%.

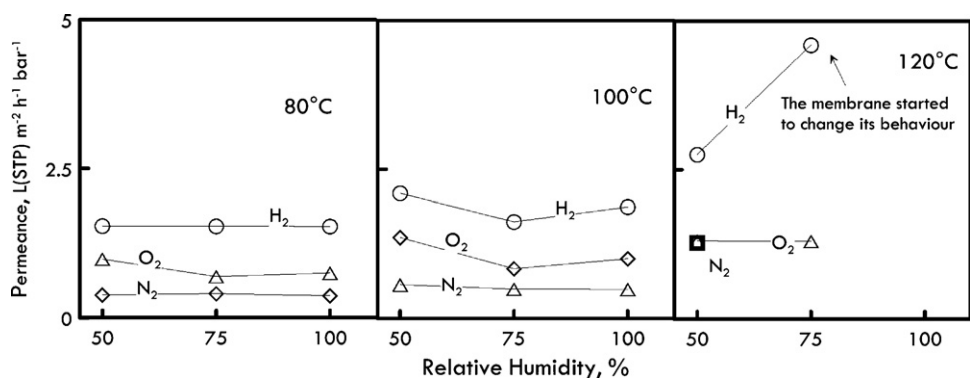


Fig. 6. Nafion 117 – H₂, N₂, O₂ permeance as a function of relative humidity, for (a) 80 °C, (b) 100 °C and (c) 120 °C.

permeance value was obtained at RH = 75% and the membrane definitely lost its barrier properties to gas permeation after 24 h in nitrogen stream at RH = 75%. The measurements achieved at 120 °C were thus affected by the changes in the conformation of the polymeric matrix.

Anyhow, as also shown by the SPEEK, the permeance of all the investigated gases increased with the temperature in the whole range of RH% (Fig. 7).

3.4. Comparison between SPEEK and NAFION 117

Owing to the difference in the thicknesses of the two membranes, the results were compared in terms of permeability instead of permeance. Globally, SPEEK showed a lower permeability than Nafion 117 at all the operating conditions investigated. This is a positive result since the lower the permeability, the lower the crossover affecting the PEMFC performance. At 80 °C the H₂

permeability of Nafion 117 membrane was higher than the SPEEK one (Fig. 8) and, showed a decrease of the permeability equally proportionate to the higher RH, whereas the Nafion 117 permeability was quite constant in the whole RH range considered. Similar trends were obtained at 100 °C. At 120 °C, the SPEEK continued to exhibit a stable trend, as the permeability lowered with the RH increase, moreover, Nafion 117 showed an unstable behaviour breaking at RH equal to 100% (Fig. 8c).

Comparing the performances of Nafion 117 and SPEEK as a function of the temperature (Fig. 9), it can be seen that the permeabilities of both membranes increased with the temperature at each RH. However, the SPEEK exhibited permeabilities always lower than Nafion 117 one. Moreover, at 120 °C, Nafion 117 showed an unstable behaviour, whereas the SPEEK was still stable.

Analyzing the results in terms of lifetime, the Nafion 117 membrane resisted 160 h and then it lost its barrier properties to gas permeation at 120 °C and 75% of RH. On the contrary,

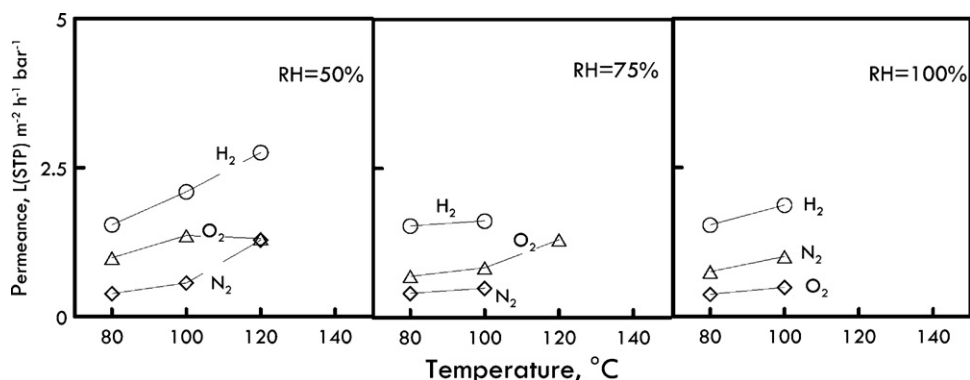


Fig. 7. Nafion 117 – H₂, N₂, O₂ permeance as a function of temperature, for (a) RH=50%, (b) RH=75% and (c) RH=100%.

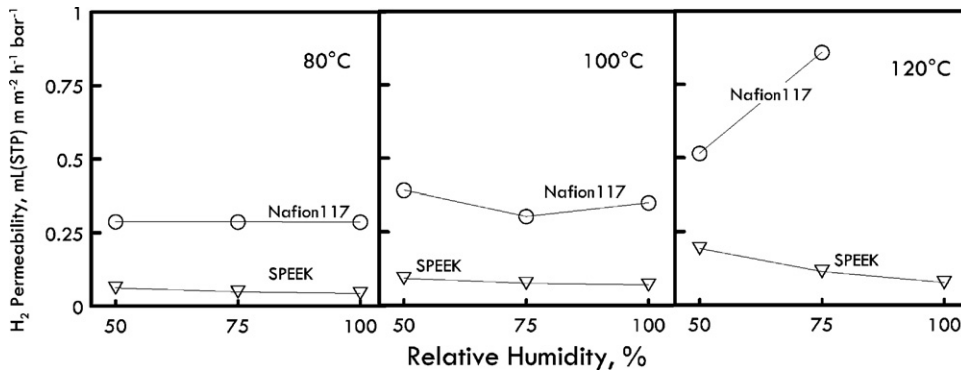


Fig. 8. H₂ permeability of SPEEK and Nafion 117 as a function of relative humidity for (a) 80 °C, (b) 100 °C and (c) 120 °C.

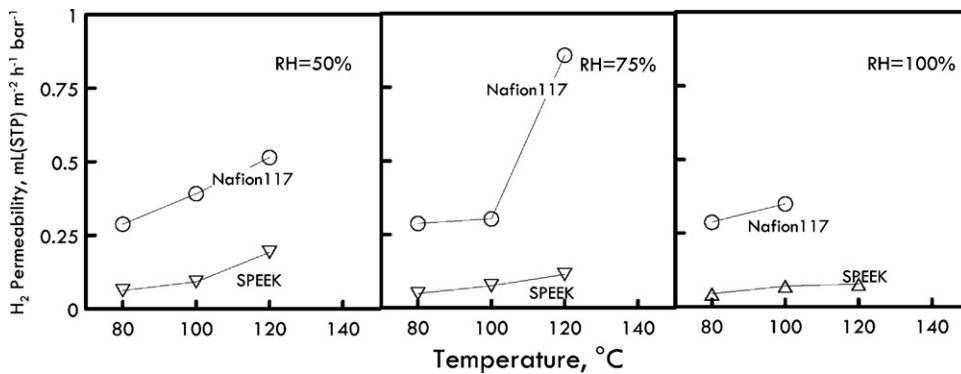


Fig. 9. H₂ permeability of SPEEK and Nafion 117 as a function of temperature, for (a) RH = 50%, (b) RH = 75% and (c) RH = 100%.

the measurements on SPEEK were stopped after 200 h and the membrane did not show any change in its behaviour, keeping its integrity.

3.5. Proton conductivity measurements

The other transport property of PEMFC is the proton conductivity. Fig. 10 shows the conductivity of a SPEEK membrane as a function of RH at 80, 100 and 120 °C. As a general trend, the conductivity increased with temperature for each RH value and depended linearly on RH at constant temperature, increasing by two orders of magnitude for RH going from 50 to 95%. On the whole, the conductivity ranged from a minimum of 0.011 S m⁻¹ at 80 °C and 50% RH to a maximum of 3.5 S m⁻¹ at 120 °C and 95% RH. In Fig. 11 the

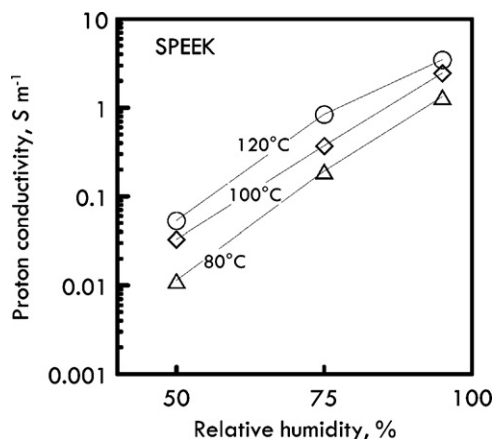


Fig. 10. Proton conductivity as a function of relative humidity measured at 80, 100 and 120 °C.

conductivity of SPEEK at 95% RH is plotted as a function of temperature and compared with the conductivity of Nafion 117 at 100% RH. The conductivity of SPEEK was lower than that of Nafion by a factor of 2–5 but increased with temperature up to 120 °C, whereas the conductivity of Nafion started decreasing above 100 °C.

3.6. New metric for the evaluation of the membrane transport properties

In the considerations related to the suitability of a membrane for high temperature PEMFC operations, usually, the proton conductivity is one of the first properties considered. A growing interest is leading also towards the evaluation of the permeation

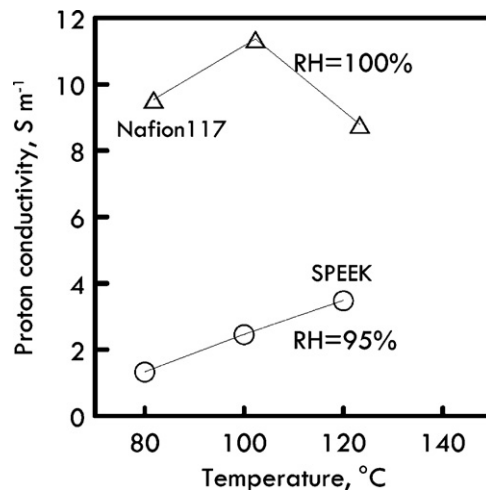


Fig. 11. Proton conductivity as a function of temperature.

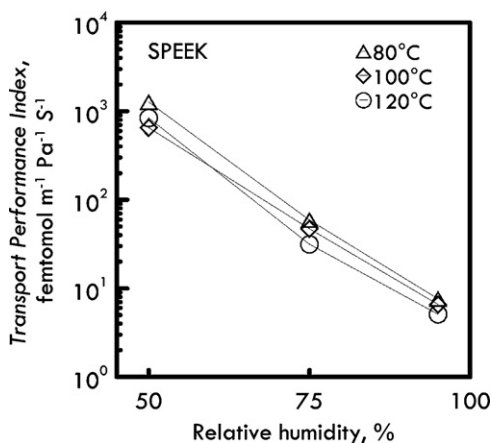


Fig. 12. Transport performance index as a function of relative humidity.

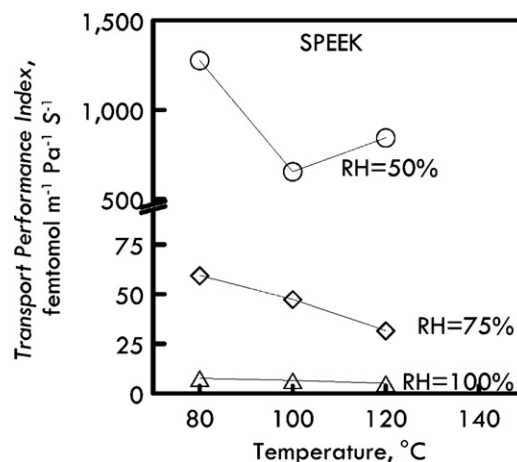


Fig. 13. Transport performance index as a function of temperature.

properties, in order to quantify also the potential crossover impact on the whole performance of the PEMFC.

In the membrane engineering approach, new indexes have been and are ongoing to be defined, to compare more than one membrane or membrane operation property, in order to have an immediate idea of the whole performance of the system. Moving in this logic, in this work, the data obtained by proton conductivity and mass transport measurements, have been compared introducing the *Transport Performance Index*, which gives an indication of the whole membrane performance in terms of transport properties and, as a consequence, of its suitability for temperature defined applications.

The *Transport Performance Index* compares the H_2 permeability of the membrane with respect to its proton conductivity. A desired membrane should exhibit a low H_2 permeability, because it means reduced crossover and, meanwhile, a high proton conductivity. Therefore, the lower the value of this index the better the membrane performances.

Transport Performance Index (TPI)

$$= \frac{2 \cdot H_2 \text{ Permeability}}{\text{Proton Permeability}}, \text{ mol s}^{-1} \text{ Pa}^{-1} \text{ S}^{-1}$$

In the following the TPI was calculated for both the membranes tested. Since two different apparatuses were used for the proton conductivity measurements, that of the SPEEK was measured at RH=95%, whereas that of the Nafion 117 was measured at RH=100% as for the permeation measurements. Even though there is this difference, however, in the calculation of the TPI we indicated a univocal RH value of 100%, assuming acceptable the error arisen from this assumption.

Fig. 12 shows the TPI of SPEEK membrane as a function of the relative humidity for three different values of temperature. In the whole temperature range, an increase of RH corresponded to a significant decrease of the TPI. This trend can be explained considering that, as it has been highlighted in Figs. 4 and 10, respectively, the permeance and, thus, the permeability of the SPEEK membrane significantly lowered equally proportionate to the higher relative humidity, whereas the proton conductivity monotonically increased.

For RH equal to 75 and 100%, any temperature increase corresponded to a reduction of the TPI and thus induced an improvement in the membrane performance, except for the RH=50% where the curve exhibited a minimum in correspondence of 100°C (Fig. 13). As a matter of fact, at this RH the increase in conductivity in the range 100–120°C was proportionally lower than the corresponding increase in permeability, thus resulting in a significant TPI increase.

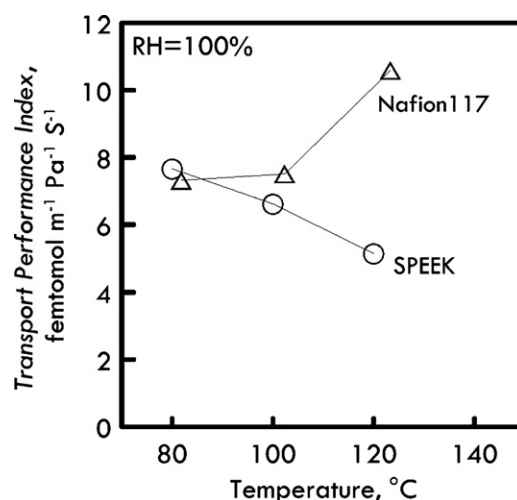


Fig. 14. Transport performance index as a function of temperature at RH = 100% for SPEEK and Nafion 117 (since the Nafion membrane broke, at 120°C its permeability was extrapolated from the other results).

The comparison of TPIs between SPEEK and native Nafion 117 (Fig. 14) highlighted the advantage offered by the SPEEK membrane. The TPI of SPEEK got the higher value at 80°C, afterwards it started to decrease as the temperature increased. On the contrary, the Nafion 117 membrane, starting at 80°C from the same value of SPEEK, exhibited an increasing trend in the whole temperature range. In addition, the TPI of the SPEEK, was always lower than the Nafion 117 one, for temperature higher than 80°C. To explain these data, it must be highlighted that even if the proton conductivity of Nafion 117 is significantly higher than the SPEEK one (Fig. 11), nevertheless, it started to reduce after 100°C. Moreover, Nafion 117 permeability was much higher too (Fig. 9). Indeed, in the comparison of the ratio of these two variables (permeability and proton conductivity), the SPEEK showed better transport properties than Nafion, particularly at a temperature higher than 100°C.

4. Conclusions

The evaluation of the mass transport properties of polymer electrolyte membranes to be used in PEMFC application is one of the most important aspects to be taken into account for the real estimation of the overall performances of the PEMFC.

In this work the mass transport properties of two different membranes, a commercial Nafion 117 and a cross linked home-made

SPEEK membrane, were measured by adopting a new approach that takes into account the strong dependence of the membrane performance on the hydrothermal history of the membrane itself. A protocol for permeation measurements was elaborated to compare the transport properties of different membranes correctly as a function of the same operating conditions. Globally, for both the membranes, the permeance of all the three gases lowered with the relative humidity, at all the temperature investigated. As a matter of fact, the SPEEK membrane showed a lower permeability than Nafion 117 at all the operating conditions investigated. This was a positive result since the lower the permeability, the lower the crossover affecting the PEMFC performance. Moreover, the Nafion 117 showed a stable behaviour up to 100 °C; the SPEEK was still stable up to 120 °C. Analyzing the results in terms of lifetime, the Nafion 117 membrane resisted 160 h and then it lost its barrier properties to gas permeation when the temperature achieved 120 °C. On the contrary, the measurements on SPEEK were stopped after 200 h and the membrane did not show any change in its behaviour, also keeping its integrity.

The other important mass transport property of the membrane to be considered together with the gas permeation properties is the proton conductivity. It was measured for both the membranes at the same operating conditions used in the permeation measurements. To relate this property to the gas mass transport, in this work a new parameter called *Transport Performance Index* has been defined as the ratio between the hydrogen permeability and the proton conductivity. The ideal/desired membrane must exhibit the lowest gas permeability and the highest proton conductivity. Therefore, the lower the value of this index, the better the membrane performances. The transport performance index of SPEEK and Nafion 117 were calculated and critically compared. It has the higher value at 80 °C for SPEEK, afterwards it started to decrease as the temperature increased. On the contrary, the value of this index for the Nafion 117 membrane is the same as that of SPEEK at 80 °C, then it increases in the whole temperature range. Indeed,

in the comparison of the ratio of these two variables (permeability and proton conductivity), the SPEEK showed better transport properties than Nafion, particularly at a temperature higher than 100 °C.

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References

- [1] <http://www.fossil.energy.gov/programs/powersystems/fuelcells/>.
- [2] J. Wu, X.Z. Yuan, J.J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, J. Power Sources 184 (2008) 104–119.
- [3] S. Zhang, X.Z. Yuan, J.N.C. Hin, H. Wang, K.A. Friedrich, M. Schulze, J. Power Sources 194 (2009) 588–600.
- [4] W. Schmittinger, A. Vahidi, J. Power Sources 180 (2008) 1–14.
- [5] S. Sugawara, T. Maruyama, Y. Nagahara, S.S. Kocha, K. Shinohra, K. Tsujita, S. Mitsuhashi, K.-I. Ota, J. Power Sources 187 (2009) 324–331.
- [6] C. Francia, V.S. Ijeri, S. Specchia, P. Spinelli, J. Power Sources 196 (2011) 1833–1839.
- [7] S.M. Javaid Zaidi, T. Matsuura (Eds.), *Polymer Membranes for Fuel Cells*, Springer, New York, 2009.
- [8] S.S. Kocha, J.D. Yang, J.S. Yi, *AIChE J.* 52 (5) (2006) 1916–1925.
- [9] H. Tang, M. Pan, S.P. Jiang, X. Wang, Y. Ruan, *Electrochim. Acta* 52 (2007) 5304–5311.
- [10] J. Peron, A. Mani, X. Zhao, D. Edwards, M. Adachi, T. Soboleva, Z. Shi, Z. Xie, T. Navessin, S. Holdcroft, *J. Membr. Sci.* 356 (2010) 44–51.
- [11] K. Broka, P. Ekdunge, *J. Appl. Electrochem.* 27 (1997) 117–123.
- [12] E. Fontananova, F. Trotta, J.C. Jansen, E. Drioli, *J. Membr. Sci.* 348 (2010) 326–336.
- [13] G. Alberti, R. Narducci, M. Sganappa, *J. Power Sources* 178 (2008) 575–583.
- [14] D.M. Xing, B.L. Yi, F.Q. Liu, Y.Z. Fu, H.M. Zhang, *Fuel Cells* 5 (3) (2005) 406–411.
- [15] M.L. Di Vona, E. Sgreccia, S. Licoccia, G. Alberti, L. Tortet, P. Knauth, *J. Phys. Chem. B* 113 (2009) 7505–7512.
- [16] M.L. Di Vona, E. Sgreccia, M. Tamilvanan, M. Khadhraoui, C. Chassigneux, P. Knauth, *J. Membr. Sci.* 354 (2010) 134–141.
- [17] M.L. Di Vona, L. Luchetti, G. Spera, E. Sgreccia, P. Knauth, *Comptes Rendus Chemie* 11 (2008) 1074.