

Oxygen and hydrogen permeation properties and water uptake of Nafion[®] 117 membrane and recast film for PEM fuel cell

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Oxygen and hydrogen permeability through Nafion[®] 117 membrane and recast Nafion film has been studied by means of gas chromatography at different values of temperature and gas relative humidity. Water uptake from the vapour phase by Nafion[®] 117 membrane and recast film has been investigated. It has been shown that oxygen and hydrogen permeability increases both with temperature and relative humidity of the gas, but water vapour uptake by both Nafion[®] 117 membrane and recast film decreased with increasing temperature. SEM studies have been performed on the membrane-electrode assembly obtained by impregnation/hot-pressing and on carbon/Nafion[®] composite; these have indicated that the active catalyst layer is porous with channels for the gas transport.

1. Introduction

In recent years fuel cells have received increased attention as an alternative power source for such terrestrial applications as local power generation and transportation since they combine high energy efficiency with pollution-free operation [1]. For electrical vehicle application, the proton exchange membrane (PEM) fuel cell is the most promising owing to its simple construction, low operation temperature (about 80 °C) and high power density [2–4].

In the PEM fuel cell, a thin organic proton conducting membrane is used as an electrolyte and a gas separator. Up to now, perfluorosulfonate polymer membrane Nafion[®] 117 from Du Pont de Nemours has been mainly used in this technology [5]. The main shortcoming of the PEM fuel cell is the high cost of the membrane and of the platinum catalyst which is necessary to obtain favourable kinetics in acid media at low temperatures. Minimization of the platinum content in the fuel cell is one of the most important prerequisites for a large scale introduction of PEM fuel cell powered vehicles.

Lately, the utilization efficiency of actual platinum content in the PEM fuel cell has substantially increased. This has been achieved by impregnating the supported Pt/C catalyst with a solution of the ionomer (Nafion[®]), which extends the three-dimensional catalyst layer (reaction zone) and increases the active platinum area [6–8].

A very important property of the Nafion[®] membrane is gas permeability, and in particular oxygen permeability, as the rate at which the reactants diffuse through the impregnated active catalyst layer may

influence the fuel cell reactions and subsequently the total performance of the fuel cell. Gas diffusion properties of the Nafion[®] membrane have been studied by several authors [9–14], often with widely differing results, and experimental conditions have been quite different from those in the real fuel cell.

Gas permeability through the membrane is a function of the relative humidity of the gas, or more precisely, water content in the membrane. Water uptake from the vapour phase is of the greatest interest as humidified gas is a principal source of membrane hydration. This water uptake has been studied by some investigators [15–19]. However, temperature ranges have been rather restricted and in many cases only values of water uptake at different water activities and constant temperature have been measured.

In our work an attempt has been made to clarify relationships between oxygen permeability, temperature and water uptake by means of measurements carried out at conditions close to those in the real fuel cell. Also, we examined the structure and gas permeation properties of the impregnated gas diffusion electrode and carbon/Nafion[®] composite.

2. Experimental details

2.1. Membranes

Commercial Nafion[®] 117 membrane and recast film obtained from Nafion[®] 117 solution were used in this study. The Nafion[®] 117 membrane was pretreated as follows [7]. It was boiled in 3% H₂O₂ solution for 1 h, and repeatedly rinsed in boiling deionized water. This

was followed by boiling in 0.5 M H₂SO₄ for 1 h and rinsed several times in boiling water. The membrane was then stored in deionized water.

Recast Nafion[®] films can be obtained by different techniques [20, 21]. We were interested in obtaining a film with properties that are close to those of the impregnated Nafion[®] layer on the electrode. For this purpose, a simple solvent evaporation technique was used that is similar to the procedure of electrode impregnation. In contrast to electrode impregnation where the amount of Nafion[®] is very small, a larger volume of 5% Nafion[®] 117 solution was placed into a Petri dish in order to obtain a sufficiently thick film that could be used for permeability and water uptake measurements. The solvent was slowly evaporated at room temperature, followed by drying at 70 °C in the air. The film obtained was swelled by adding a small amount of deionized water and after that it was peeled off. The film was kept in a desiccator over silica gel as it was brittle and sensitive to prolonged exposure to water. For the same reason no pretreatment similar to that of commercial Nafion[®] 117 membrane was performed.

2.2. Permeability measurements

Permeability measurements were made by means of the equipment shown in Figs 1 and 2. The cell was constructed as follows. The membrane sample was sandwiched between two stainless steel plates (Fig. 1), each having a gas inlet and outlet as well as gas chambers facing the membrane. Oxygen or hydrogen was supplied to the left chamber and helium to the right chamber of the permeability cell. One of the cell outlets led to the gas chromatograph, the other one to the beaker with distilled water (Fig. 2). In this way, there was the same pressure in the two gas chambers and possible effect of pressure gradient and convection was excluded. All gases were humidified in gas wash bottles. The temperature of the gas wash bottles, as well as of the cell, was held constant by means of water thermostats. Relative humidity of the gases was changed by using a temperature difference between the humidifiers and the thermostated cell. For experiments with dry gas, the wash bottles were removed from the system and the membrane

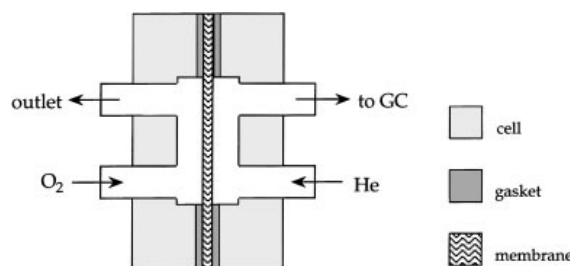


Fig. 1. The cell used for permeability measurements.

sample was dried in vacuum before the experiment. Before each experiment the cell containing the sample was equilibrated with the gas at a given temperature and relative humidity for at least 6 h. The amount of oxygen or hydrogen diffusing through the membrane was determined by measuring respective concentration in the outlet gas from the right chamber by means of a gas chromatograph, Hewlett Packard 5890 Series II. The software used was HP Chemical Station. The oxygen signal was rather small and sometimes differed from sample to sample or day to day. To obtain more pronounced relationships between permeability and temperature or relative humidity, series of measurements at different temperature or relative humidity were usually performed for the same membrane during several days.

An impregnated electrode (E-TEK, Inc. Pt content 0.35 mg cm⁻²) for permeability studies was obtained as follows. It was impregnated by 5% solution of Nafion[®] 117 and dried according to the procedure used for making membrane-electrode assemblies.

2.3. Water uptake measurements

To determine membrane water uptake from the vapour phase the sample was exposed to water vapour with 100% relative humidity at a given temperature for several days. During the experiment the sample weight was measured and after its stabilization the water content was determined by weighing the sample and subtracting the weight of the dry sample. Water uptake measurements were repeated for different membrane samples. The heat-treated membrane sample was obtained by drying under vacuum at

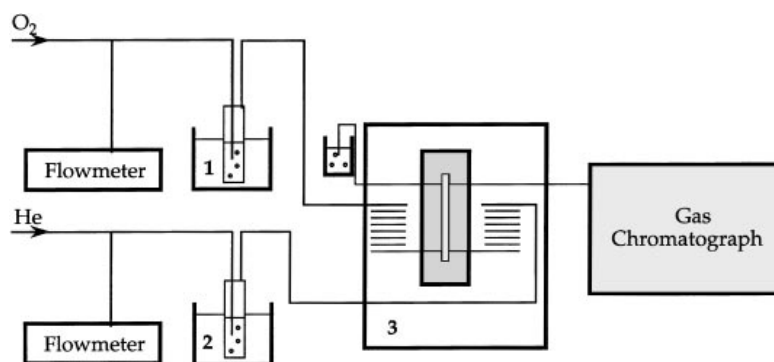


Fig. 2. The equipment for permeability measurements: 1, 2 - thermostatic gas humidifiers, 3 - thermostatic permeability cell.

room temperature for 16 h followed by drying in the oven at 120 °C for 5 min.

2.4. SEM studies

Scanning electron microscopy (SEM) studies were performed on the membrane–electrode assembly and the Nafion[®]/carbon composite. Membrane–electrode assembly was obtained by a procedure similar to those described in [22, 23]. Electrodes were impregnated by Nafion[®] 5% solution by brushing technique, dried and hot-pressed to the purified membrane at a temperature of 125 °C and a pressure of 50 atm under a period of 1 min. The Nafion[®]/carbon composite was obtained as follows. Nafion[®] 5% solution and carbon powder was mixed in ultrasonic bath and then allowed to dry in a Petri dish at room temperature for 24 h. Drying was completed in the oven at 70 °C. In this way a thin and brittle Nafion[®]/carbon film was obtained that could be easily fractured into smaller fragments for use in the SEM study. Samples of the membrane–electrode assembly were prepared by freeze-fracturing or freezing followed by cutting with a glass knife. The microscope used was a Jeol JSM-5400 scanning electron microscope.

3. Results and Discussion

3.1. Membrane water content

The curves for water vapour uptake by Nafion[®] 117 membrane and recast Nafion[®] film at 100% relative humidity and different equilibration temperatures are shown in Fig. 3. Data presented were obtained from different runs and for different pieces of membrane. Before the measurement the membrane was predried in vacuum at room temperature. Some measurements

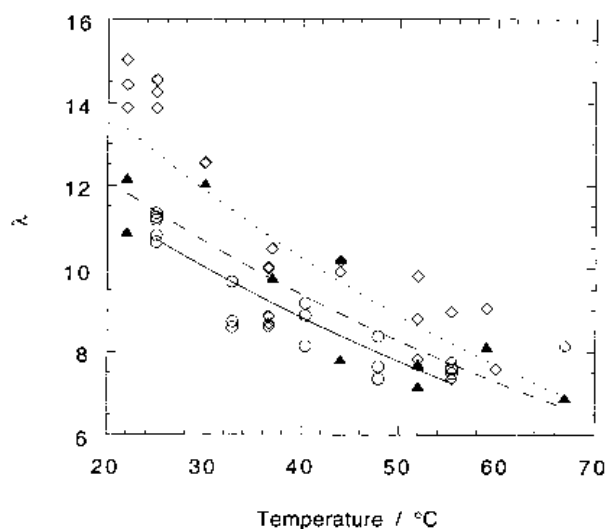


Fig. 3. Water uptake from vapour phase (100% relative humidity) by Nafion[®] 117 membrane and recast film at different equilibration temperatures: (◇) Nafion[®] 117 membrane, (▲) recast Nafion[®] film, (○) heat-treated Nafion[®] 117 membrane. Fitted curves: second order polynomial; λ : number of water molecules per one sulfonate site.

were performed with wet membrane. Comparison of the results showed that both pretreatment procedures led to the same water uptake values. For both Nafion[®] 117 membrane and recast film, water uptake decreased with increasing temperature, and it was slightly lower for recast film over the whole temperature range. Water uptake decreased dramatically in the temperature region 25–50 °C and continued to diminish slower with increasing temperature. The lower water uptake at higher temperatures has already been reported by other investigators [15, 16]. Hinatsu *et al.* [15] have published a water sorption isotherm for Nafion[®] 117 at 80 °C that showed lower water uptake values at 80 °C (10 water molecules per sulfonic group at 100% relative humidity) than those for 18–30 °C reported in literature [17]. Lower water uptake by Nafion[®] at elevated temperatures has also been reported by Rieke *et al.* [16], who had measured water content by spectroscopic technique at 30, 50, 75 and 95 °C. According to their data the water content was highest at 30 °C (15 water molecules per sulfonic group) and lower at 50, 75 and 95 °C (9, 6 and 11, respectively). Unfortunately, the equipment used by us did not allow measurements at temperatures higher than 70 °C.

Membrane water uptake from the liquid phase was examined for several membrane samples and the values obtained was about 21 which is consistent with the data published earlier [15, 19]. It can be seen that the values for liquid water uptake are higher than those for water vapour. The explanation for this phenomenon, known as Schroeder's paradox [24], was discussed by Zawodzinski *et al.* [17], who considered the difficulty in condensing vapour within the pores of the membrane as a possible reason for lower water uptake from the vapour phase. As proposed by Hinatsu *et al.* [15], condensation of vapour within pores might be even more difficult at elevated temperatures, and because of this the water uptake decreases when the temperature of the vapour increases.

According to some authors, the membrane is dried under vacuum before the hot-pressing of the electrodes in order to avoid shrinking under the hot-pressing procedure. These treatments may possibly influence the water uptake, and in order to clarify this, a heat-treated sample of Nafion[®] 117 membrane was examined. Results obtained are shown in Fig. 3, where they are compared with water uptake data by the ordinary sample. It can be seen that the water uptake by the heat-treated sample is lower than that by the untreated Nafion[®] membrane. A possible explanation is an irreversible reorganization of the membrane structure and changes in the size of the ionic clusters, which occur under the heat treatment of the membrane and influences water uptake properties.

3.2. Permeability measurements

Oxygen permeability as a function of temperature and relative humidity of the gas is shown in Figs 4

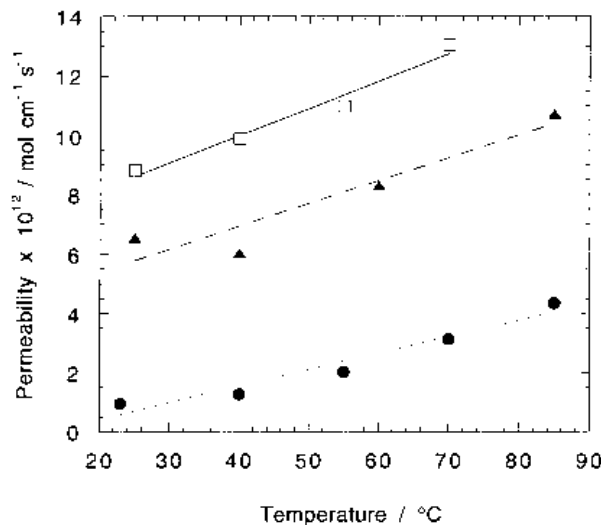


Fig. 4. Oxygen permeability through the Nafion[®] 117 membrane and recast film at different temperatures: (□) Nafion[®] 117 membrane, 100% relative humidity, (▲) recast Nafion[®] film, 100% relative humidity, (●) dried Nafion 117 membrane, dry gas. Straight lines are obtained by the least-square method.

and 5. As seen from Fig. 4, the permeability increased with the temperature for all samples studied. To illustrate the importance of gas humidity, an experiment with dry gas and dry Nafion[®] membrane was carried out that showed remarkably lower permeability values than those for humidified gas. The influence of relative humidity of the gas is also seen in Fig. 5, where permeability is measured as a function of relative humidity. It should be noted that it was difficult to obtain good reproducibility for different series of oxygen permeability measurements (i.e. for different membrane samples and different occasions). Figure 6 shows an example from two different runs where a shift between two straight lines representing the permeability temperature relationship for oxygen can be seen. A possible explanation of this problem is that the values of permeability are rather low (and therefore, the amounts of oxygen registered by the

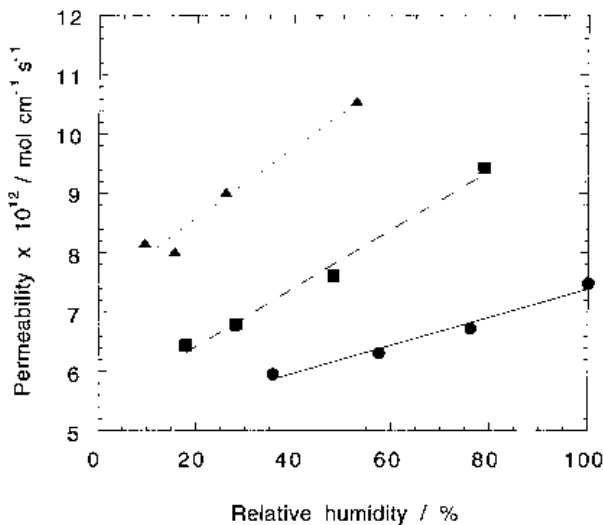


Fig. 5. Oxygen permeability through the Nafion[®] 117 membrane at different values of gas relative humidity: (▲) at 80 °C, (■) 60 °C, (●) 40 °C.

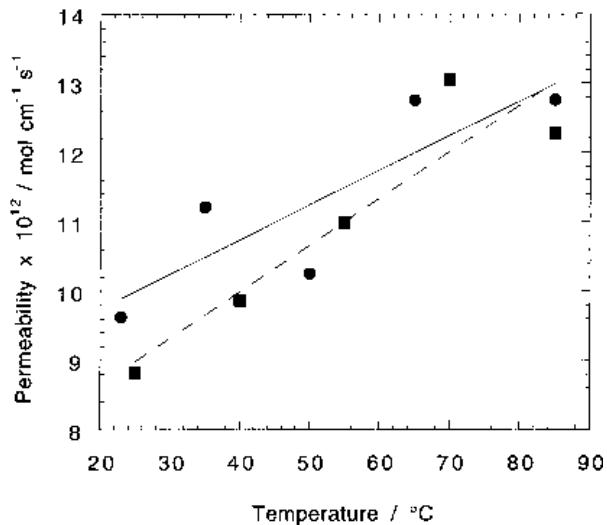


Fig. 6. Two different series of oxygen permeability measurements through the Nafion[®] 117 membrane.

gas chromatograph are very small), and minor deviations in experimental conditions like atmospheric conditions in the laboratory, small differences in membrane pretreatment may influence the results. Another possible reason is be insufficient equilibration with water vapour. This is, however, a point of discussion since the preliminary permeability tests showed that the amount of oxygen diffusing through the membrane becomes constant after 5–6 h of measurement. The value of permeability was nearly the same regardless of the initial condition of the membrane (dried or fully hydrated). Another suggestion regarding membrane equilibration with water vapour is that there exist small deviations in water uptake for different membrane samples and this factor can also influence the permeability values. In spite of the scatter in the values of permeability, the relationships between permeability and temperature or gas relative humidity are sufficiently pronounced to be used both qualitatively and quantitatively. Figures 7 and 8 show hydrogen permeability through the

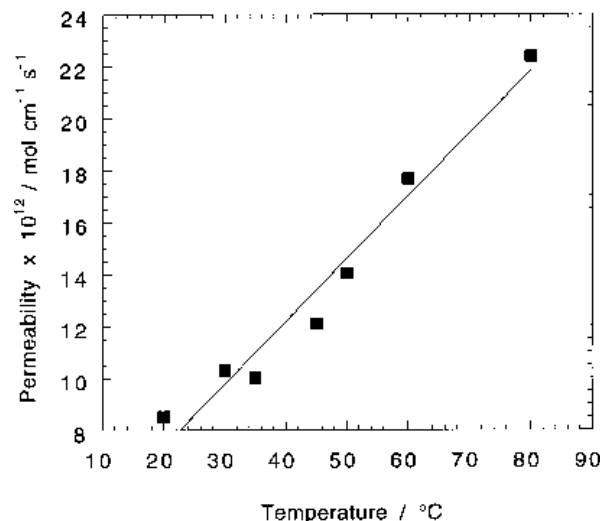


Fig. 7. Hydrogen permeability through the Nafion[®] membrane at different temperatures.

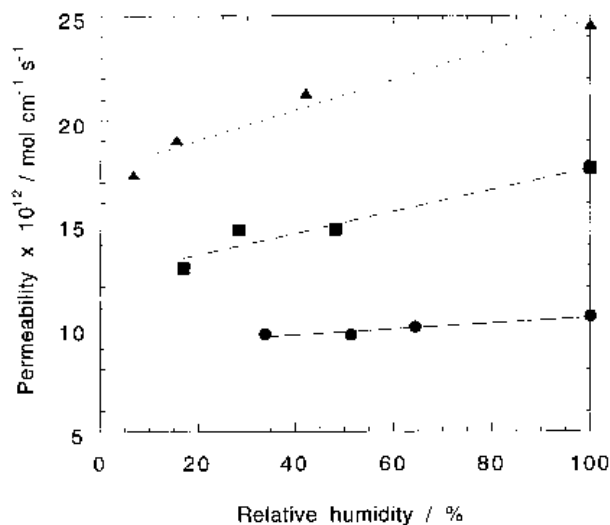


Fig. 8. Hydrogen permeability through Nafion[®] 117 membrane at different values of gas relative humidity: (▲) at 80°C, (■) 60°C, (●) 40°C.

Nafion[®] 117 membrane as a function of temperature and relative humidity. As in the case of oxygen, the permeability increased with both temperature and relative humidity, but the values for hydrogen were about twice those for oxygen.

The permeability of oxygen through the Nafion membrane has been studied by several researchers [9–14] and different values of permeability coefficients have been obtained. When discussing permeability, authors often refer to the structure model described by Yeager *et al.* [25, 26] who distinguished three different parts of the Nafion[®] structure, namely, rigid hydrophobic backbone, flexible perfluorocarbon and hydrated ionic cluster region. In the papers mentioned above various mechanisms of oxygen permeation and Nafion[®] areas involved have been suggested.

According to Sakai *et al.* [12] the permeability of oxygen through the Nafion[®] membrane increased with the water content. This was explained by the fact that the diffusion coefficient of oxygen increased with the water content since it is considerably higher in water than in hydrophobic media such as polytetrafluoroethylene (PTFE). On the other hand, the solubility of the oxygen is higher in PTFE than in water, but according to [12] it decreased only a little (the permeability of the gas through a nonporous membrane is a product of solubility and diffusivity $P = D \times S$). On the basis of these results, Sakai stated that the gas mainly permeates through the hydrated ion clusters of the polymer and connecting channels.

Ogumi *et al.* [11] discussed the permeability of oxygen through the Nafion[®] in terms of Yeager's structural model of the Nafion[®] [25]. According to Ogumi permeation of gases took place in the amorphous region and permeation through ionic clusters was very small.

The present results showed that both relative humidity and temperature markedly influenced the values of permeability. Increase of permeability with

relative humidity suggests an interaction of the gases with water-containing ionic clusters that might lead to the conclusion that the permeation of gases occurs in the cluster region. On the other hand, water acts as a plasticiser in the polymer increasing the diffusion coefficient of the permeate. Thus, swelling of Nafion[®] may result not only in the increase of the size of ionic clusters but also in dimensional changes of the whole polymer. Due to this property, increase of permeability with increasing temperature does not exclude gas transport through the hydrophobic region of Nafion[®]. According to the results obtained, permeability of oxygen increases with temperature at constant values of relative humidity both for dry and hydrated Nafion[®] membrane as expected from the results of other investigators [10–12, 14]. At the same time, results from water uptake measurements (Fig. 3) show that the membrane water uptake decreases with increasing temperature, and the highest values of permeability in the case of hydrated membrane were obtained when the membrane water content was lowest. This observation can hardly be explained by gas transport exclusively through ionic clusters. Obviously, the amorphous hydrophobic region is also an important part of the membrane for oxygen transport and the mechanism of gas permeation is rather complex, involving both hydrated ionic clusters and hydrophobic amorphous region of Nafion[®].

Figure 4 shows that the values of permeability for recast Nafion[®] film were slightly lower than those for the commercial Nafion[®] membrane. Several authors have already pointed out differences in properties and morphology between commercial Nafion[®] membranes and recast films [20, 21]. One of the most important features of the recast film is absence of a crystalline phase which, according to Moore *et al.* [20] leads to higher water uptake and lower permselectivity. Increase of the ratio between amorphous and crystalline phases could be a reason for higher gas permeability as according to several concepts [9, 11], gases permeate mainly through the amorphous hydrophobic region of Nafion[®]. Also, the crystalline region increases the barrier for water-induced swelling [21], and taking this into account, water uptake by the recast polymer can be expected to be higher than that of the commercial film. However, it was not the case in our experiments, where commercial Nafion[®] and recast film had rather similar values for water content and oxygen permeability (they were slightly lower for the recast film). Obviously, the method used for the preparation of the recast film preparation can influence the properties remarkably. The film obtained by us had a lower value of water uptake which probably accounts for the slightly lower oxygen permeability as the last increases with relative humidity of the gas (membrane water content is known to increase with relative humidity at constant temperature [17]).

The impregnated active catalyst layer is of greatest importance in the fuel cell. It seemed to be valuable to test if the impregnated Nafion[®] solution forms a thin

film on the electrode surface and if the rate of gas transport is limited by oxygen permeation through the impregnated Nafion[®] layer. Results obtained showed that oxygen transport through the impregnated electrode was very fast and in a short time oxygen was equally distributed between the two cell chambers. This was a case even after repeated impregnation. It leads to the conclusion that the impregnation of the electrode does not involve formation of a thin Nafion[®] film on the electrode surface. It is more likely that platinum agglomerates are only partially covered by Nafion[®] and pores for gas transport remain open. This finding is of interest for mathematical modelling of the PEM fuel cell as both pseudohomogeneous film [27–29] and agglomerate [30] concepts appear in the models of the active catalyst layer. The microstructure of the catalyst layer will be discussed below on the basis of SEM studies.

The membrane–electrode assembly can also be obtained by another method [31], where Nafion[®] solution is mixed with catalyst particles (Pt on C) and hot-pressed to the membrane, and the uncatalysed electrode is used as a gas diffusion backing. Nafion[®]/carbon composite obtained by us was very brittle and not suitable for permeation measurements. To investigate its structure with respect to gas transport properties, a SEM study was performed.

3.3. SEM study

A SEM study was carried out for the membrane–electrode assembly and the Nafion[®]/carbon composite. These two samples were chosen in order to illustrate the structure of the active catalyst layer for membrane–electrode assemblies obtained by two different techniques: electrode impregnation with Nafion[®] solution and hot-pressing to the Nafion[®] membrane [22], and mixing of Nafion[®] solution with catalyst particles and hot-pressing to the membrane (uncatalysed carbon paper or carbon cloth is later used as a gas diffusion backing) [31]. Figures 9 and 10 show parts of the membrane–electrode assembly where the membrane is hot-pressed to the im-

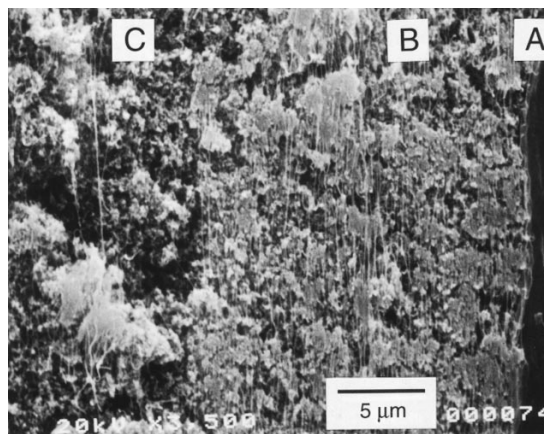


Fig. 10. Cross section of the membrane–electrode assembly (cut by glass knife): (a) Nafion[®] 117 membrane, (b) impregnated active catalyst layer, (c) electrode.

pregnated electrode. The SEM micrographs show very good attachment between the electrode and the membrane. For the sample obtained by knife cutting, the impregnated Nafion[®] layer appears as shorter ‘fibres’ (Fig. 10) partially incorporated into the structure of the active catalyst layer. The impregnated electrode remains porous and permeable for gases, which is in agreement with permeability measurements discussed above. Impregnated Nafion[®] layer is more clearly distinguished in the SEM micrograph of the sample that was prepared by cutting by glass knife and Nafion[®] fibres were stretched along the cut surface. For comparison a micrograph of recast Nafion[®] film was taken (Fig. 11) that appeared to be dense and uniform. Another SEM micrograph of the Nafion[®]/carbon composite (Fig. 12) represents another technique of manufacturing membrane–electrode assemblies (in our case carbon powder is used instead of carbon supported Pt catalyst). It can be seen that the structure of composite is very porous which suggests good gas transport through it and explains its pure mechanical properties. The microstructure of the active layer of two kinds of the membrane–electrode assemblies supports the idea stated on the basis of

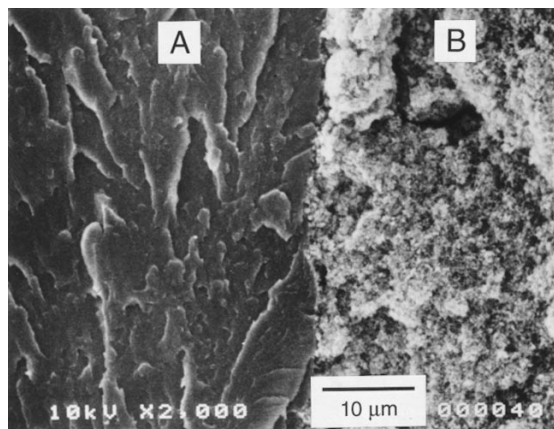


Fig. 9. Freeze-fractured cross section of the membrane–electrode assembly: (a) Nafion[®] 117 membrane, (b) impregnated active catalyst layer.

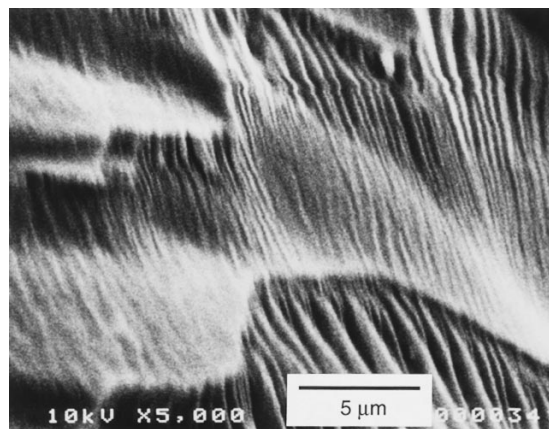


Fig. 11. Freeze-fractured cross section of the recast Nafion[®] film.

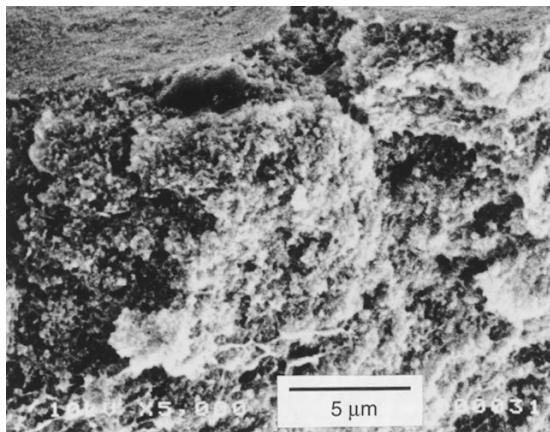


Fig. 12. Fractured cross-section of the Nafion[®]/carbon composite.

permeability measurements that the agglomerate structure model of the catalyst layer is a better representation of the reaction zone than the film model.

4. Conclusions

The water uptake from vapour phase by the commercial Nafion[®] 117 membrane and recast Nafion[®] film was determined. It decreased with increasing temperature and was slightly lower for the recast film. Water uptake by a heat-treated Nafion[®] membrane was examined and it was lower than those by the untreated sample and the recast film. Oxygen permeability measurements were carried out for the commercial Nafion[®] 117 membrane and recast film at different values of temperature and gas relative humidity. Permeability increased with temperature and relative humidity for both forms of Nafion[®] studied and, similarly to water uptake, it was slightly lower for the recast film. Hydrogen permeability was examined for the commercial Nafion[®] 117 membrane, and it was about two times higher than oxygen permeability. Relationships permeability–temperature and permeability–relative humidity suggested that both hydrophobic and hydrated cluster regions were important for oxygen transport in Nafion[®] as the values of permeability were highest at 80–85 °C, when the membrane water content was lowest, and, at the same time, permeability increased with relative humidity (and membrane water content) at a given temperature. SEM study of the membrane–electrode assembly and the carbon/Nafion[®] composite showed that in both cases the active catalyst layer remained porous and permeable for gases.

Acknowledgements

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