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SWELLING BEHAVIOUR OF PEMFC DURING CONDITIONING

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Abstract - Polymeric cation exchange membranes (PEMFC) are used in fuel cell technology. These membranes act as a physical barrier between anode and cathode, but diffusion through the membrane should allow protons to be carried from anode to cathode at a rate sufficient to supply energy requirements. They avoid any direct reaction of oxygen and hydrogen that would diminish fuel cell efficiency. Membranes have to be conditioned before use. This conditioning step changes membrane counterions and modifies their water content, which has an effect on their diffusion coefficients. In order to analyse and quantify the effect of conditioning techniques on membrane performance various experiments with Nafion 117 cation exchange membranes were carried out. Membranes were conditioned using various methods to change the charged cation in the membrane. The reactives used were ultrapure water, nitric acid, hydrochloric acid, hydrogen peroxide, sodium chloride, potassium chloride and ethylene glycol, all at room temperature. Some conditioning methods were carried out using solvents heated to 100 ºC. Water content was indirectly monitored by measuring membrane swelling. Results show that membrane conditioning with strong acids followed by treatment with water increases membrane water content by about 5%. Using high-temperature treatment the water content also increases. Water uptake or release from membranes is analysed in terms of water activity.
Keywords: PEMFC; Cation exchange membrane; Swelling; Conditioning method; Fuel cell.

INTRODUCTION

The conditioning method used on perfluorinated polymeric membranes is very important in terms of fuel cell performance. These membranes can be found in different states, classified by Berezina et al. (2002) as normal, shrunk and extended: "normal" is the typical state for the end product; the shrunk state is achieved after boiling in salt solutions and finally the extended state is achieved after sequential boiling steps in acids and distilled water.

There is also a superextended state that can be achieved when the membrane is brought into contact with ethylene glycol at 110 ºC. The water content of the membrane is usually defined by the molar ratio of water to the functional group. In the case of the superextended state this value can be as high as 36 mol H_2O/mol SO^{3-}, but the normal content does not usually exceed 16 mol of water/mol SO^{3-}.

Exchange membranes have been applied in many fields, such a dialysis, electrodialysis and, more recently, polymer electrolyte fuel cells (PEMFC).

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Organic cation exchange membranes were first used in 1959 by William T. Grubbs. He tried to provide an ion conductive gas barrier to separate hydrogen and oxygen compartments inside a fuel cell (Grune, 1992).

Current environmental legislation is very restrictive, so new technologies are being developed. This is the case with polymer electrolyte fuel cells, which are efficient and environmentally clean electricity generators. All the research work done in this direction is on catalyst performance, operation conditions and the mechanism of transport through the membrane. In ion exchange resins some studies have been carried out into the swelling /shrinking behaviour of the resin beads during the ion exchange process, and here it is proposed to carry out the same study on water content ratio and membrane swelling.

Andersson et al. (1998) analyse the swelling kinetics of ion exchangers using a microscope and a video camera to determine the effective diffusion coefficient. They also take temperature changes into account. Their results are used to simulate the swelling/shrinking process.

The general objective of this work is to measure the volume variations in a perfluorinated ion exchange membrane during the conditioning, so as to record the behaviour with different ions and to monitor elastic behaviour over several cycles of the swelling/shrinking of the membrane. From these data sets a comparative study of the swelling of the membrane is carried out by assessing the ion load versus the polymer volume. Several systems have been studied by this method, all of them single cation aqueous systems.

METHODS

Characterization of the Membrane

The microstructural morphology of the membrane surface is examined by SEM-EDX without using any etching procedures. The microstructure is made apparent by using secondary electrons and backscattered images.

Samples must be treated for correct observation and characterisation, and this procedure is especially important if their composition or microstructure is liable to be modified during observation.

First, the membrane is introduced into a CEA 035 diode sputter coating device. Here the sample is coated with carbon or gold, depending on whether it is being treated for microscope observation or microanalysis. Then microanalysis and structural examination are carried out in a JEOL 6400 coupled with an energy dispersive x-ray spectrophotometer, EDX link EXL and WDX JEOL.

By means of this technique a picture of the membrane cross section is obtained using backscattered electron techniques. To verify the quantity of cations inside the membrane the EDX technique is used.

TGA measurements are used to determine the amount of water molecules next to the internal structure of the membrane. For this purpose a SETARAM TG-DSC 111 thermobalance with a linear ramp of 5ºC per minute was used.

The membrane was used as supplied at the beginning of each experiment (potassium form). A piece measuring 2×2 mm^2 was cut out with a scalpel and placed inside the microreactor, where the swelling of the membrane was monitored by a video camera connected to a computer with an image processing program. On the computer the thickness of the membrane was continuously reported.

The microreactor (shown in Figure 1) designed by Mijangos and Ortueta (1998) was mounted under an optical microscope with the video camera. Measurements of variations in membrane thickness (swelling/shrinking) throughout the cycle are more reliable, since human error is avoided. The experimental error associated with thickness measurements is $\pm$ 0.05 μm for the 95% confidence level.

The ion exchange capacity of the membrane was measured by potentiometric titration. For this purpose the membrane was first treated with HCl 0.1 M. After washing with ultrapure water, 0.18 M NaOH was added using an automated burette that adds 0.2 mL of base every 300 seconds.

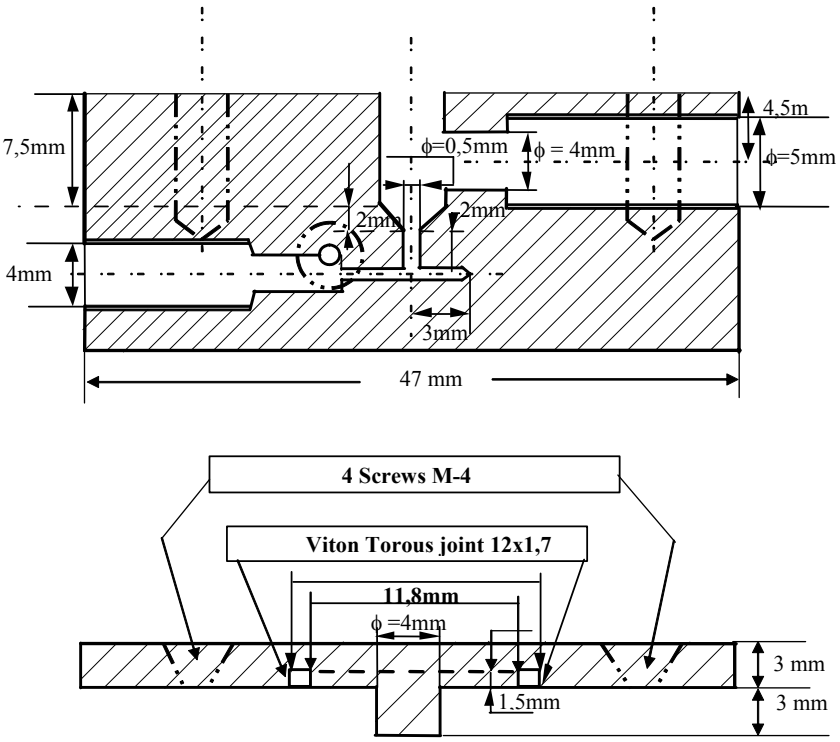

Figure 1: Optical cell used to measure the swelling/shrinking of the membrane.

Swelling Pressure and Hydration Number Calculations

Cation exchange membranes are able to sorb solvents in which they are placed. While taking up solvent, the matrix expands. Swelling equilibrium is a balance of opposing forces: the tendency of ionic constituents of the membrane to surround themselves with solvent and the resistance of the polymeric matrix to the uptake of more water. The water inside the cation exchanger membrane is subject to contractive forces due to elastic forces of the polymeric matrix and thus is under higher pressure than the external water surrounding the membrane. The pressure difference between the internal and external water is called swelling pressure and can be calculated using the following equation:

$$\Pi v_w = -RT \ln a_w \tag{1}$$

where Π is the swelling pressure; v_w, the partial molar volume of the solvent; R, the gas constant; T, the absolute temperature; and a_w, the activity of water in the membrane. Thermodynamic equilibrium is achieved when chemical potential inside is equalled to that outside the membrane, and hence water activity is the same inside and outside of the membrane electrolyte solution. Water activity is calculated from the lowering of water vapour pressure in the solution in accordance with the following equation:

$$a_w = \frac{P_w}{P_w^0} \tag{2}$$

where P_w is the partial pressure of water and P_w^0 is the partial pressure of pure water at the temperature of the experiments.

From the volume variation of the membrane the water molecules next to the functional group are calculated as the hydration number by the following equation:

$$n = \frac{\left(m_o + \frac{\Delta V}{V_w}\right)}{Q_a \; M_W} \tag{3}$$

where Q_a is the acid-base ion exchange capacity, n is the hydration number, m_o is the initial water content inside the membrane, ΔV is the variation of the membrane volume, V_w is the partial molar volume of the water and M_w is the molecular weight of water.

Swelling Measurements

The membrane used in this study is an anisotropic membrane. When this membrane is immersed in a solvent it swells more in one direction than in the others. To study this behaviour several experiments measuring volumetric variation in all three spatial directions were carried out. Two parameters are used to characterise these variations:

$$H_z = \frac{\gamma}{\sqrt{\alpha\beta}} \quad \text{and} \quad H_{xy} = \frac{\alpha}{\beta} \tag{4}$$

where

$$\alpha = \frac{\Delta x}{x_o} \quad \beta = \frac{\Delta y}{y_o} \quad \gamma = \frac{\Delta z}{z_o} \tag{5}$$

A schematic of the volume variations undergone by the membrane is shown in Figure 2.

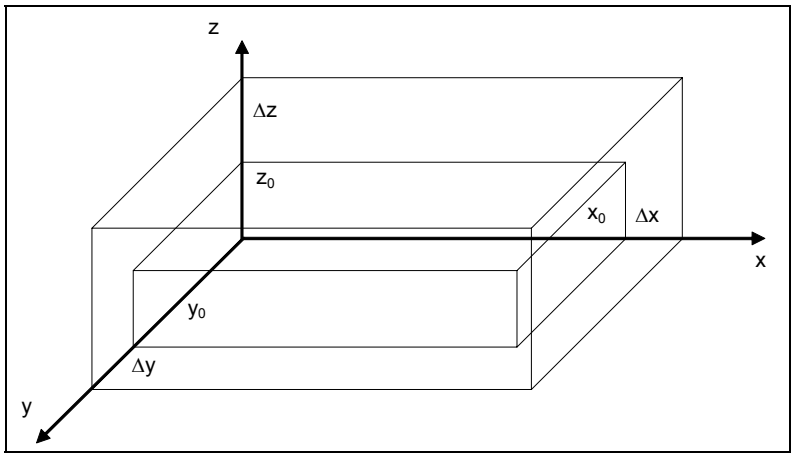

Figure 2: Membrane swelling in all three spatial directions.

RESULTS AND DISCUSSION

The experiments were carried out at room temperature and 100 ºC. Most of the conditioning methods found in the bibliography, such as conditioning with KCl, NaCl and HCl, are applied at room temperature, but some are applied at 100 ºC using HNO_3 and/ or H_2O_2 and the conditioning method with polyethylene glycol is applied at 60 ºC and 110ºC. The treatment with solvents and salts changes the properties of the membrane swelling or shrinking the polymeric matrix. An example of the kinetic behaviour for a treatment with hydrogen chloride is shown in Figure 3; as can be seen the swelling is fast, taking place in 20 to 30 seconds.

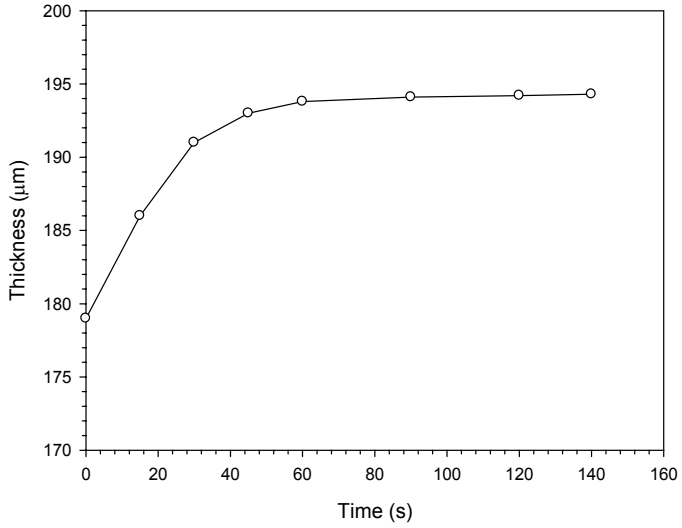

Figure 3: Swelling kinetics for the treatment with HCl.

Effects of the Different Conditioning Methods on the Membrane Structure

Variations in membrane thickness were measured at each step of an operational cycle. As supplied, the membrane is in the potassium form and in order to make sure that all the functional groups are in the potassium form the membrane was treated with KCl. The first step of this conditioning cycle is to bring it into contact with a 2 M KCl solution. In this step the membrane thickness decreases by 1% within the first 30 seconds after contact and thereafter remains constant. Subsequently 0.2 M KCl solution was used for 200 seconds, as shown in Figure 4: in the first 30 seconds the membrane swelled about 1 μm. The next step was to bring the membrane into contact with 0.06 M KCl. This caused it to swell again to its initial dimensions. Finally a cleaning step was applied in which the membrane was brought into contact with ultrapure water for a further 200 seconds. In this step the membrane swelled slightly. This cycle was repeated three times on the same membrane sample.

Figure 4 also summarises the changes in thickness undergone by the membrane along with the results obtained with analogous treatments with KCl, NaCl and HCl.

As can be seen in Figure 4, there is considerable swelling of the membrane depending on the counterion: this is due to the different water activities of the ionic solutions. When the membrane is treated with HCl (2 M, 0.2 M, 0.06 M) the thickness of the membrane increases by 10 % of the initial figure. When the membrane is treated with NaCl (2M, 0.2M, 0.06 M) the variation in thickness is lower, but still significant, at 5.5% of the initial thickness. But when it is treated with KCl (2M, 0.2M, 0.06 M) there is no variation in thickness. The ionic form supplied is potassium. This was also tried using SEM-EDX analysis, as shown in Figure 5. The EDX analysis shows the presence of a large amount of potassium in the membrane.

A microphotograph of the membrane (Figure 6) was also taken in order to show the internal structure. The membrane has a homogeneous structure in accordance with the manufacturer's specifications.

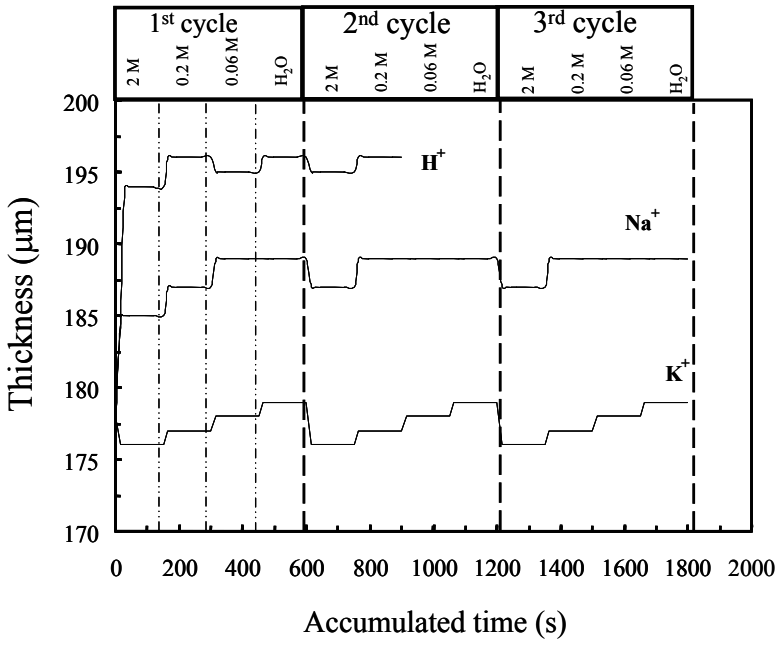

Figure 4: Variations in thickness of the membrane using different counterions.

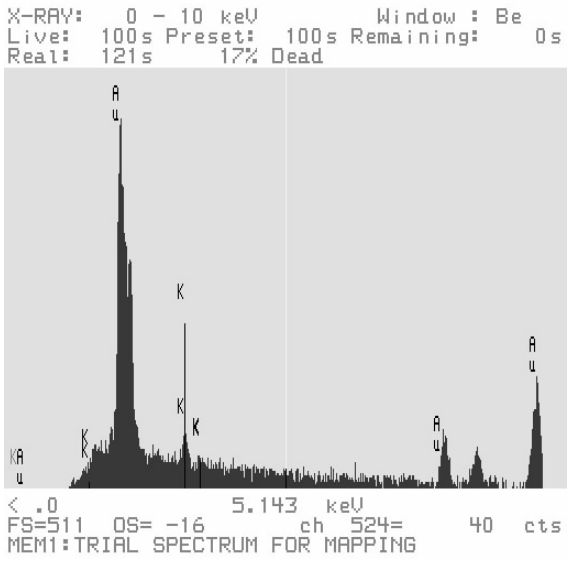

Figure 5: EDX analysis of the Nafion 117 membrane in the supplied form. (-SO_3 K)

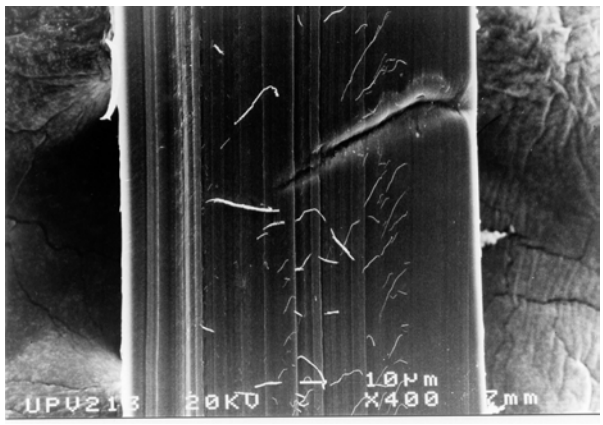

Figure 6: Microphotograph of a Nafion 117 membrane in the supplied form.

Volume Variations and Swelling Pressures

Using equations 1 to 3 for the different conditioning methods, the difference in swelling pressures inside the membrane were calculated. The data obtained are shown in Tables 1 to 3. Table 1 reports the results for the KCl conditioning method, where an increase in the hydration number (water content of the membrane) occurs while the swelling pressure decreases. The membrane water content increases when the opposing forces decrease because of matrix elasticity. In the second and third cycles the same behaviour is observed, but the differences are smaller.

As can be seen in Table 2, a change in the counterion results in a different swelling pressure, mainly due tothe different water activities of the solutions. Replacing potassium by sodium causes a change in the swelling pressure and a considerable change in the hydration number.

In the case of conditioning with nitric acid with heat treatment (Table 3) at 100 ºC, the internal structure of the membrane matrix is completely changed. Because of this the elastic forces of the polymeric matrix decrease, increasing the uptake of water, so the hydration numbers (water content) are higher than in the sodium and potassium conditioning methods. The variation in swelling pressure is low due to the low concentration of the acid.

The hydration number ranges between 4 and 17 mol water per mol of sulphonic group, which is in agreement with the chemical structure reported in the relevant literature (Berezina et al., 2002).

The other parameter studied in this work during conditioning is the anisotropic behaviour of the membrane, as explained in section 2.3 above. The figures measured for the sodium conditioning method calculated in accordance with equations 4 to 6 are shown in Table 4.

The effects studied in this work are not related to Donnan exclusion (which has no influence on swelling behaviour), but the affinity of ions for functional groups (lyotropic series) is related to the interaction of cations or anions with the fixed groups inside the ion exchange material (or polymer electrolyte membrane). Each ion carries a hydration shell that enters the matrix depending on the affinity of the ion for the fixed group.

As can be seen in Table 4, the swelling behaviour is not the same for the three spatial dimensions (see Figure 2). From H_{xy} we can say that the membrane swells more in the x direction than in the y direction. But in the case of H_z, as the value is approximately one, the relative swelling in the z direction is the same as the geometrical mean of the relative swellings of x and y.

Table 1: Swelling pressures and hydration numbers during conditioning cycles using different KCl electrolyte solutions.

Cycle	Solution	Π–Π'(atm)	*n*
1st	initial	0	
	KCl 2M	-87.5	3.7
	KCl 0.2M	-8.4	4.3
	KCl 0.06M	-2.3	5.1
	H_2O	0	5.5
2nd	initial	0	5.5
	KCl 2M	-87.5	4.7
	KCl 0.2M	-8.4	5.2
	KCl 0.06M	-2.3	5.5
	H_2O	0	5.9
3rd	initial	0	5.9
	KCl 2M	-87.5	5.1
	KCl 0.2M	-8.4	5.5
	KCl 0.06M	-2.3	5.7
	H_2O	0	6.0

Table 2: Swelling pressures and hydration numbers during conditioning cycles using different NaCl electrolyte solutions.

Cycle	Solution	Π–Π'(atm)	*n*
1st	initial	0.0	
	NaCl 2M	-94.8	6.7
	NaCl 0.2M	-9.2	7.8
	NaCl 0.06M	3.1	8.8
	H_2O	0.0	8.8
2nd	initial	0.0	8.8
	NaCl 2M	-94.8	8.0
	NaCl 0.2M	-9.2	8.8
	NaCl 0.06M	-3.1	8.8
	H_2O	0.0	8.8
3rd	initial	0.0	8.8
	NaCl 2M	-94.8	8.8
	NaCl 0.2M	-9.2	8.8
	NaCl 0.06M	-3.1	8.8
	H_2O	0.0	8.8

Table 3: Swelling pressures and hydration numbers during conditioning cycles using HNO_3 0.025M at 100ºC.

Cycle	Solution	Π–Π'(atm)	n
1st	initial	0.0	
	HNO_3 0.025M	-1.5	13.5
	H_2O	0.0	15.1
	H_2O	0.0	15.7
2nd	initial	0.0	15.7
	HNO_3 0.025M	-1.5	15.3
	H_2O	0.0	16.2
	H_2O	0.0	16.4
3rd	initial	0.0	16.4
	HNO_3 0.025M	-1.5	16.5
	H_2O	0.0	16.5
	H_2O	0.0	16.6

Table 4: Anisotropic behaviour of the membrane using the NaCl conditioning method.

Cycle	Solution	Hz	Hxy
1st	NaCl 2M	1.00	0.82
	NaCl 0.2M	1.01	0.80
	NaCl 0.06M	1.06	0.77
	H_2O	1.06	0.77
2nd	NaCl 2M	0.97	0.81
	NaCl 0.2M	1.07	0.77
	NaCl 0.06M	1.06	0.77
	H_2O	1.06	0.77
3rd	NaCl 2M	0.96	0.81
	NaCl 0.2M	1.06	0.77
	NaCl 0.06M	1.06	0.77
	H_2O	1.06	0.77

CONCLUSIONS AND FINAL REMARKS

Nafion membranes display an elastic behaviour that is closely related to the counterion loaded within the matrix structure and with external solution characteristics. This behaviour is relevant for their application to PEMFC technology for optimised operating results.

On the other hand, these membranes show a very clear anisotropic behaviour, with swelling/shrinking being clearly different in the three spatial directions. Swelling is higher in the x direction (transverse direction TD) than in the y direction (machine extrusion direction MD). The relative swelling in the z direction (perpendicular to the membrane plane) is nearly the same as the geometrical mean of the relative swellings of x and y.

A change in the counterion changes the water content and swelling pressures inside the polymeric matrix because of the differences in water activities (osmotic pressure) between the ionic solutions.

Treatment with acids and heat changes the physical properties of the polymeric matrix, increasing the uptake of water by the membrane. The treatment decreases the elastic forces of the matrix, decreasing the swelling pressure and hence increasing the water content of the PEM.

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