Swelling properties of alkali-metal doped polymeric anion-exchange membranes in alcohol media for application in fuel cells

L. Laín, V. M. Barragán*

Department of Applied Physics I,
Faculty of Physics, University Complutense of Madrid,
28040 Madrid, Spain.

*Corresponding author. Fax: +34913945191; e-mail: vmabarra@ucm.es

ABSTRACT

Swelling properties of four commercial anion-exchange membranes with different structure have been analyzed in several hydro-organic media. With this target, the liquid uptake and the surface expansion of the membranes in contact with different pure liquids, water and alcohols (methanol, ethanol and 1-propanol), and with water-alcohol mixtures with different concentrations have been experimentally determined in presence and in absence of an alkaline medium (LiOH, NaOH and KOH of different concentrations). The alkali-metal doping effect on the membrane water uptake has also been investigated, analyzing the influence of the hydroxide concentration and the presence of an alcohol in the doping solution. The results show that the membrane structure plays an essential role in the influence that alcohol nature and alkaline media has on the selective properties of the membrane. The heterogeneous membranes, with lower density, show higher liquid uptakes and dimensional changes than the homogeneous membranes, regardless of the doping conditions.

Keywords: Anion-exchange membrane, swelling properties, doping capacity; alkaline fuel cell; alcohol

1. Introduction

Fuel cells directly convert chemical energy into electrical energy and provide an attractive alternative power source. Among the various types of fuel cells, the direct alcohol fuel cells (DAFCs) have advantages that include high energy density, low emission of pollutants, and the ability to use liquid fuels, with a broad range of applications as portable electronic equipment and biomedical devices [1]. To overcome the drawbacks of acid fuel cells using proton-exchange membranes, alkaline fuel cells (AFCs) using solid anion-exchange membranes evoked great interest. AFCs present advantages as better corrosion resistance and faster kinetics of oxygen reduction reactions in an alkaline media, which allows the use of non-noble catalysts [2]. The use of anion-exchange membranes as solid polymer in AFCs avoids the problems of the liquid electrolyte. In addition, the water management is improved due to the electro-osmotic drag transporting water way from the cathode to the anode reducing the alcohol crossover problem [2-4].

Currently interest in technologies utilizing anion-selective membranes is rapidly increasing [4-8], not only in relation to alkaline fuel cell and water electrolysis, but also in areas of water treatment and food industry, electrodialysis and electrodeionization, energy storage and recovery [9-13]. For these reasons, properties of anion-exchange membranes have recently received an increasing attention in order to obtain better anion-exchange membranes for increasing the performance of solid alkaline direct alcohol fuel cells (SADAFCs) [14,15], as well as for comparing them with cation exchange membranes to be applied in SADAFCs [3,16-18].

As compared with their counterparts –cation-exchange membrane, anion-exchange membranes are an emerging technology that offers the promise of reducing the catalyst cost, while achieving high power density of direct alcohol fuel cells. Hence, the understanding of water transport properties through this new type of membranes becomes essential [15]. The DAFC operated in the hydroxide-conduction mode offers a cost advantage, especially on polymer electrolyte and catalysts compared to the analogous proton exchange mode [19]. When $(OH)^-$ ions are present in the fuel stream, comparison between an alkaline and an acidic direct alcohol fuel cell, both using the same catalyst, indicates a better performance of the former, independently of the type of fuel [2]. It has recently been demonstrated that, even using existing ion conductors and catalysts, an addition of an alkali (NaOH or KOH) to ethanol would enable anion-exchange membrane direct ethanol fuel cell attribute to the added base [16].

As the core component of an alkaline anion-exchange membrane fuel cell, the electrolyte membrane plays a vital role in determining the cell performance. For this reason, numerous efforts have been made during the last few years to develop efficient alkaline anion-exchange membranes (AAEMs) for application in AFCs. Still, commercial AFCs appear to be in their early stages of developed [6]. AAEMs must possess high hydroxide conductivity, dimensional and mechanical stabilities. Two main problems, however, remain to be solved, namely low hydroxide conductivity and insufficient chemical stability against alkali attack at elevated temperature [7].

The question of what type of membrane is more suitable in SADAFCs with an added base remains unclear. A porous structure into a polymeric membrane creates more open paths as well as higher surface area for ion transfer and the absorption of an electrolytic solution. The enhancement of electrolytic solution absorption and water uptake significantly help the increase of ionic conductivity [20]. Cross-linking and reinforcement can restrain membrane swelling and improve tensile strength of the membrane. It is also beneficial for the chemical stability of AAEMS [7].

Research is needed in the aspects of characterizing of AAEM properties, including water uptake. Solvent uptake properties of the membrane are very important because the transport behaviour is closely dependent on the amount of absorbed liquid. Since water is also known to assist the mass transport of alcohol and oxygen in a fuel cell, the solvent uptake measurement could serve as a quantitative measure of membrane performance for DAFC application as well.

Hence the objective of this work was to make a systematic comparison of different heterogeneous and homogeneous polymeric anion-exchange membranes in alcohol media with an added base, and when membranes are doped by different hydroxide solutions and alcohols, in terms of membrane swelling properties.

2. Material and methods

2.1. Materials

Four different commercial anion-exchange membranes were tested in this study. Ralex membranes, AM(H)-PES (hereafter named PES) and AM(H)-PP (hereafter named PP), Neosepta AMX membrane (hereafter named AMX), and Fumasep FAP-450 (hereafter named FAP). Some of their main properties are given in Table 1.

Table 1- Properties of the used membranes.

Membrane	***d*** **(µm)***	**IEC (meq g^{-1})**	**Selectivity***	**Electric* Resistance (Ω cm^2)**	***ρ*** **(kg m^{-3})****
PES	450	1.8	> 0.95	< 7.5	945
PP	440	1.8	> 0.95	< 8.0	917
AMX	140	1.5	≥ 0.98	< 3.5	1090
FAP	50	1.2	> 0.92	< 1.5	1132

*Provided by the manufacturer [21-24].
**Measured.

PES and PP membranes are composites formed from ion-exchange resins with polyethylene basic binder on base quaternary ammonium. Both membranes have different reinforcing material, PES membrane is a polyester fitting fabric and PP is a polypropylene fitting fabric. AMX membrane is composed of a styrene divinylbenzene copolymers with tri-alkyl ammonium fixed charge groups. It contains a reinforcing inert mesh. FAP membrane is a non-reinforced, fluorinated anion exchange membrane. Figure 1 shows the basic chemical structure of a quaternary ammonium-type anion-exchange membrane and of a fluorinated-type anion-exchange membrane.

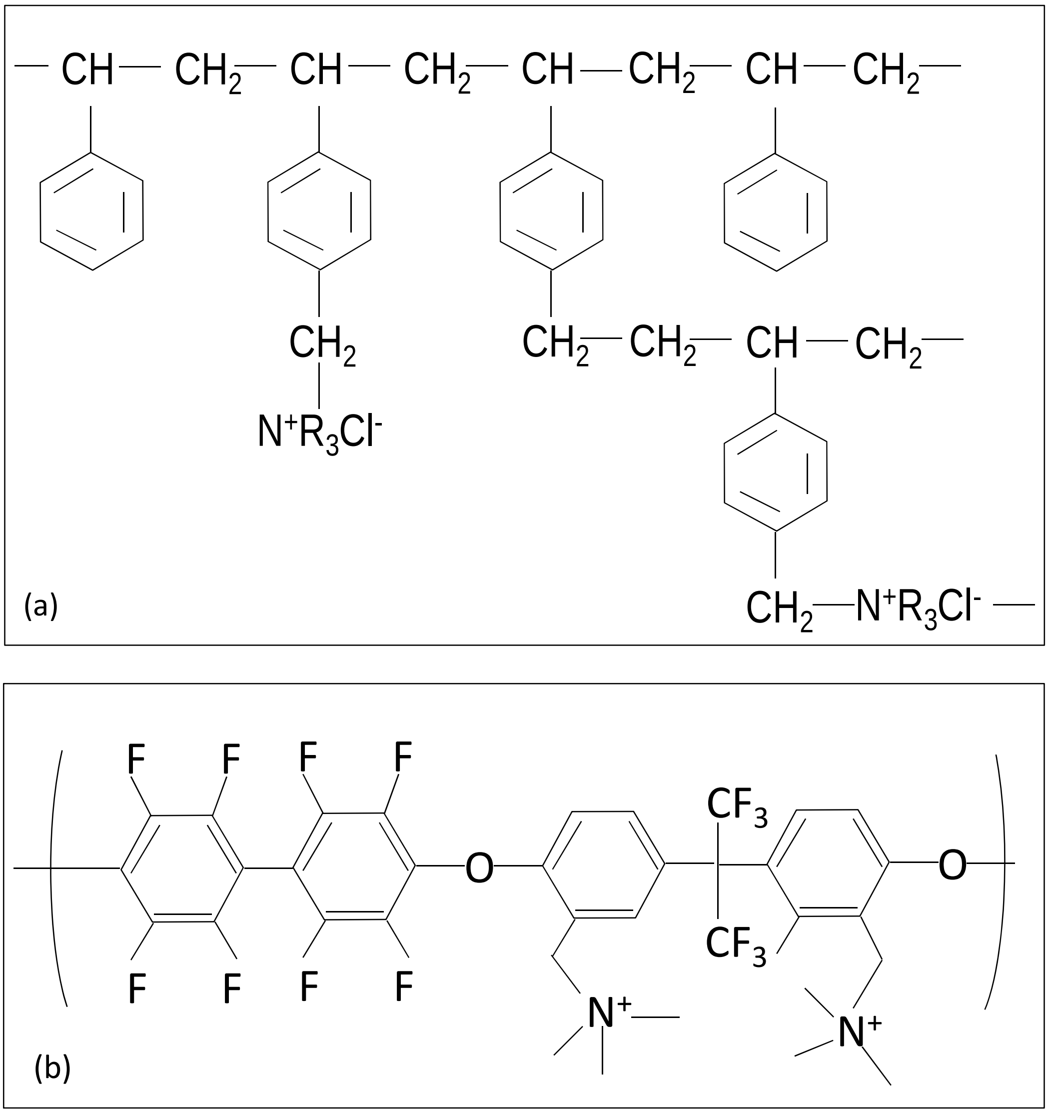

Fig. 1- Typical chemistry structure (a) of a quaternary ammonium-type anion-exchange membrane (Neosepta AMX membrane), (b) of a fluorinated-type anion-exchange membrane.

The membranes can be divided with respect to their structure and preparation into two categories: Ralex PES and PP membranes are considered as heterogeneous membranes, whereas AMX and FAP are considered as homogeneous membranes. Membranes were used as received, without any previous treatment.

The materials used in the experiments were water, methanol (MeOH), ethanol (EtOH) and 1-prophanol (1-PrOH) as pure liquids, and water-alcohol mixtures of 1M and 2M concentration as solvents. Table 2 shows some properties of the pure liquids and mixtures used as solutions.

Table 2- Density (ρ), viscosity (ν), and molar mass (M) of the used pure liquid, and density (ρ) and viscosity (ν) of the used water-alcohol mixtures at 303 K.

Pure Liquid		**ρ (kg m^{-3})***	**ν^* (mPa s)**	**M (10^{-3}kg mol^{-1})**
Water	H_2O	995.7	0.797	18.0
MeOH	CH_4O	782.0	0.508	32.04
EtOH	C_2H_6O	781.3	0.987	46.07
1-PrOH	C_3H_8O	796.4	1.726	60.09
Water-Alcohol Mixture		**ρ (kg m^{-3})***	**ν^* (mPa s)**	
1M	**MeOH**	999.2	0.756	
	EtOH	976.4	0.709	
	1-PrOH	990.2	0.920	
2M	**MeOH**	984.7	0.939	
	EtOH	973.2	1.258	
	1-PrOH	982.9	1.100	

(*)[25,26]

LiOH, NaOH and KOH of 1M and 2M concentrations were used as alkaline salts. Pure pro-analysis grade chemicals and doubly distilled, degassed pure water were used.

2.2. Methods

2.2.1. Solvent uptake and doping capacity

The solvent uptake of the membranes in the different solutions was determined using the traditional gravimetric method. Before the experiments, the membrane samples were dried under vacuum for 24 h and weighted in a high precision balance (±0.0001g). After that, the samples were immersed in closed bottles containing the corresponding solution and allowed to equilibrate at 30 ºC. After 48 h of immersion the swollen membranes were taken out from the solutions, wiped carefully with filter paper in order to remove remained water drops, and weighted again. The increase in weight was equal to the weight of the liquid absorbed by the membrane. The solvent uptake was calculated from the weight of the swollen and dry membrane samples according to the expression [27]:

$$S(\%) = \frac{m_w - m_d}{m_d} \times 100 \tag{1}$$

where m_w and m_d are the masses of the swollen and dry membrane, respectively. The reproducibility of the measurements was checked in all cases.

The solvent content of the membrane can also be expressed as the average number of molecules per conducting functional group, λ, determined by [28]

$$\lambda = \frac{S}{100\ \mathrm{IEC}\ M_w} \tag{2}$$

where IEC represents the ion-exchange capacity (*i.e.* the ionizable hydrophilic functional groups content per gram of polymer, eqg^{-1}), and M_w is the molecular weight of the corresponding liquid.

To measure the membrane alkaline doping capacity, *AU*, the membranes were removed from the concentrated alkaline solution and washed in deionized water for several times to remove the free alkali remained in the membrane. Afterwards, the membranes were dried under vacuum for 24 h and weighted. The doping capacity was estimated as [29]:

$$AU(\%) = \frac{m_{OH-d} - m_d}{m_d} \times 100 \tag{3}$$

where m_{OH-d} is the mass of the corresponding dry doped membrane.

2.2.2. Dimensional change

The parameter considered to estimate the dimensional change of the membranes was the area of the surface sample. To determine the membrane surface expansion, samples of surface, A_d, approximately square about 30x30 mm^2 were used. The procedure was similar to the one used for determining the solvent uptake, but in this case, the length of the two sides of the sample was measured. The surface expansion was calculated from the change of the area according to the following expression:

$$EA(\%) = \frac{A_w - A_d}{A_d} \times 100 \tag{4}$$

where A_w and A_d are the areas of the swollen and dry membrane, respectively.

The reproducibility of the measurements was checked in all cases.

2.2.3. Porosity and Flory-Huggins (FH) interaction parameter

The membrane void porosity φ (volume of free solution within the membrane per unit volume of wet membrane) can be expressed as a function of the solvent uptake S as follows [30]:

$$\varphi = \left[1 + \frac{100\rho_l}{S\rho_m}\right]^{-1} \tag{5}$$

where ρ_m and ρ_l are the densities of the dry membrane and the sorbed liquid, respectively.

The analysis of the sorption properties of the membranes in a pure liquid can also be made using a model derived from the Flory-Huggins (FH) theory [31], which makes a statistical calculation of the different configurations of a polymer/liquid system upon some assumptions on molecular shapes and interactions. The model enables sorption modelling using a single parameter, the so-called FH interaction parameter, which is a reflection of the polymer/liquid affinity. The lowest FH parameter values describe the highest liquid sorption level and, thus the best affinities. The FH interaction parameter can be estimated from the membrane void porosity as:

$$\chi = -\frac{\ln \varphi + (1-\varphi)}{(1-\varphi)^2}. \quad (6)$$

2.2.4. Volumetric charge fixed concentration

In some cases, the value of IEC is not particularly useful to characterize how a membrane works, because it doesn’t consider the membrane swelling properties. A more appropriate measure of the true concentration of fixed charge groups is the volumetric fixed charge concentration of membrane immersed in the dissolution, $\overline{X}$. This value depends on both membrane and medium, and it can be estimate from the IEC, water uptake and density of the membrane and the density of the solvent, by means of the expression [31]:

$$\overline{X} = \frac{\mathrm{IEC}}{\frac{1}{\rho_m} + \frac{S}{100\rho_l}}. \quad (7)$$

3. Results and discussion

3.1. Non-doped membranes in non- electrolyte solution

3.1.1. Swelling properties

Liquid uptake and surface expansion have been measured for all the investigated membranes in the different pure liquids and alcohol-water mixtures. To check the stability of the swelling properties, the time evolution of the mass and dimensions of the membrane was analyzed. To this purpose the mass and surface area of the swollen membranes were measured once a day during a minimum of a week. The results showed that both mass and dimension of the samples reached stable values from 48 h after the immersion in the corresponding solution. The values corresponding to the last day measurement were used to estimate membrane solvent uptake and surface expansion. Results are shown in Table 3. The error in the measurement of solvent uptake and surface expansion was lower than 2% in the most unfavorable case.

Table 3- Liquid uptake and surface expansion for the different membranes used in pure liquid and water-alcohol mixtures of different alcohol concentration.

Membrane		**PES**		**PP**		**AMX**		**FAP**	
		S (%)	*EA* (%)	***S*** (%)	*EA* (%)	***S*** (%)	*EA* (%)	***S*** (%)	*EA* (%)
Pure liquids									
	Water	53	11	58	11	21	14	7	5
	MeOH	43	5	44	12	23	14	22	21
	EtOH	36	8	37	16	18	15	37	16
	1-PrOH	36	3	38	15	22	11	32	16
Water-Alcohol Mixtures									
1M	**MeOH**	58	10	60	11	18	5	11	4
	EtOH	58	7	62	11	19	10	7	12
	1-PrOH	61	7	63	8	21	11	12	8
2M	**MeOH**	57	8	60	8	28	14	13	12
	EtOH	61	5	63	15	25	14	17	11
	1-PrOH	64	9	66	11	23	17	13	8

Solvent uptake properties of the membrane are very important because the performance of a membrane is dependent on counter-ion conductivity, which is turn of depend of its solvent content [3].

As can be observed, both heterogeneous membranes presented similar values of the solvent uptake, although slightly higher for membrane PP, probably due to its lower density. In the case of pure liquid, a decrease of the liquid uptake was observed with the alcohol viscosity. With water-alcohol mixtures, the opposite behavior was observed. Solvent uptake increased when alcohol size and concentration increased. Thus, solvent uptake was always higher with mixtures than with the corresponding pure liquids. The influence of the alcohol nature was higher at higher alcohol concentrations. This results were also observed with cation heterogeneous membranes [32].

Homogeneous membranes presented lower solvent uptakes than heterogeneous membranes. For membrane AMX, the influence of the liquid nature was low, in agreement with previous results [3]. In the case of membrane FAP, a significant decrease of liquid uptake was observed in water with respect to alcohols. This effect could be due to the interactions between liquid and membrane and the absence of a reinforcing in the membrane structure.

The surface expansion for both heterogeneous membranes in pure liquids revealed a similar value immersed in water but a different behavior in presence of alcohols. For membrane PES the expansion was under the value of water and for membrane PP the values of expansion for alcohols are over the water value. This may be due to the different reinforcing material of both membranes, which is basically the unique difference between membranes PES and PP. In case of homogeneous membranes and pure liquids, the solvent nature hardly influences on the membrane expansion for membrane AMX, whereas the expansion was higher with pure alcohol than with water for membrane FAP, with a trend to decrease with mixtures.

It was observed that the expansion was slightly higher in one of the dimensions of the sample, so that some anisotropy in the dimensional change was observed for the heterogeneous membrane PP in pure liquids, decreasing this effect in the case of mixtures. This anisotropy has also been observed with other membranes in the literature [30,33,34], probably due to the orientation of polymer chains toward the drawing direction [34]. Membrane PES did not present any anisotropy, which would indicate that the different behavior may be due to their different composition of the fitting fabric. For homogeneous membrane, only FAP membrane showed a slight anisotropy with pure liquids. Membrane AMX presented scarcely anisotropy. This membrane incorporates a PCV fabric as matrix reinforcement [35] which could explain the limited influence of the solvent nature.

For heterogeneous membranes, no clear relationship between the liquid content and surface expansion or significant influence of the medium nature was observed. This may be explained taking into account the porous structure of the less dense heterogeneous membranes. In these membranes, the absorbed liquid would occupy the membrane cavities, and a distension of the polymeric chains of the matrix would be not required. It would explain the low expansion observed for these membranes in spite of their large liquid uptake. However, for homogeneous membranes, with higher density, the absorbed liquid should break through the interstices of the membrane, so it would expected higher expansions at lower solvent uptakes. This effect should be larger with not reinforced, FAP membrane as it has been observed.

3.1.2. Porosity, Flory-Huggins (FH) interaction parameter and fixed charge concentration

The membrane void porosity and the FH interaction parameter were estimated for all the membranes according to Eqs. (5) and (6). The results obtained for pure liquids and alcohol-water mixtures are shown in Tables 4 and 5, respectively. The corresponding volumetric fixed charge has been also estimated from the values of solvent uptake and by using the corresponding density values shown in Tables 1 and 2, in agreement to Eq. (7). The results are also shown in Tables 4 and 5.

Table 4- Porosity (φ), FH interaction parameter (χ), parameter λ, and volumetric fixed charge $\overline{X}$ (mol dm^{-3}) of anion exchange membranes used in this study in pure liquids.

	Membrane															
	PES				**PP**				**AMX**				**FAP**			
Liquid	φ	χ	λ	$\overline{X}$	φ	χ	λ	$\overline{X}$	φ	χ	λ	$\overline{X}$	φ	χ	λ	$\overline{X}$
Water	0.33	0.97	16	1.13	0.35	0.95	18	1.07	0.19	1.31	8	1.37	0.07	1.97	3	1.26
MeOH	0.34	0.96	7	1.12	0.34	0.96	8	1.09	0.25	1.14	5	1.27	0.24	1.15	6	1.03
EtOH	0.30	1.02	4	1.19	0.30	1.03	5	1.15	0.20	1.26	3	1.35	0.35	0.95	7	0.89
1-PrOH	0.30	1.03	3	1.19	0.31	1.02	4	1.14	0.23	1.18	2	1.30	0.31	1.00	4	0.93

Table 5- Porosity (φ) and volumetric fixed charge $\overline{X}$ (mol dm^{-3}) of the different membranes used in water-alcohol mixtures of different alcohol concentrations.

Water-Alcohol Mixture		**Membrane**							
		PES		**PP**		**AMX**		**FAP**	
		φ	$\overline{X}$	φ	$\overline{X}$	φ	$\overline{X}$	φ	$\overline{X}$
1M	**MeOH**	0.35	1.10	0.36	1.05	0.15	1.40	0.09	1.21
	EtOH	0.36	1.19	0.37	1.04	0.16	1.39	0.06	1.25
	1-PrOH	0.37	1.07	0.38	1.04	0.17	1.37	0.11	1.19
2M	**MeOH**	0.35	1.10	0.37	1.06	0.21	1.29	0.11	1.18
	EtOH	0.37	1.09	0.38	1.03	0.20	1.32	0.14	1.14
	1-PrOH	0.38	1.05	0.39	1.02	0.18	1.35	0.11	1.18

The results in Table 4 show that for homogeneous and heterogeneous membranes the affinity grows with the porosity in all cases. As it would be expected, heterogeneous membranes with pure liquids present higher porosity and affinity having the larger value for membrane PP immersed in water (the lowest value of χ). An exception it is observed with membrane FAP and EtOH, which presents similar values than the heterogeneous membranes. The results of Table 5 reveal an increase of porosity proportional to the concentration and the size of the alcohol. Higher porosities were observed for mixtures with respect to pure liquids for heterogeneous membranes, whereas the opposite trend was observed in the case of homogeneous membranes.

The values of the fixed charge concentration are of the order of 1-1.5 eq dm^{-3}, typical values in this kind of membranes [3]. They are higher for homogeneous membranes, as it is expected from their lower solvent uptakes. Heterogeneous membranes presented, in general, higher values with pure alcohol than with water, while the opposite behavior was observed for homogeneous membranes. With water-alcohol mixtures, the observed trend was higher values for the lower alcohol concentration with a later increase with increasing the alcohol concentration. This behavior was more pronounced with 1-PrOH and homogeneous membranes.

As the fixed charge concentration is an indicative of the membrane selectivity, these results would indicate that at alcohol concentrations typical in direct alcohol fuel cells, membranes would increase their selectivity, with exception of 1-ProOH.

3.2. Alkali-metal-doped membranes

The membrane doping capacity was estimating according to the method described in section 2.2.1. To determine the water uptake, *WU*, of the doped membranes, the dry doped samples were immersed in deionized water at 30 ºC for 48 h. After hydration, the surface water was wiped with tissue paper before weighing. Then, the membranes were fully dried in a vacuum oven for 48 h and weighing again. Water uptake was estimated from Eq. (1) where m_w and m_d correspond in this case to the masses of the swollen and dry doped membranes, respectively. Results obtained for doping capacity and water uptakes are shown in Tables 6 to 9. The stability was checked in a similar way tan for non-doped membranes.

Higher values of water uptake were found for the doped heterogeneous membranes, showing the heterogeneous membrane PES the highest values. When heterogeneous membranes were doping in aqueous solutions, no clearly define trend was observed with the type and concentration of electrolyte. Membranes doped with LiOH presented the highest values and the lowest values were observed with NaOH. When alcohol was presented in the doping solution, lower water uptakes were observed in general, but the influence of the type and concentration of electrolyte depended on the type and concentration of alcohol, being this behavior similar for both heterogeneous membranes. For heterogeneous membranes, a relative reduction of water uptake higher than 50% can be gotten with the doping process, depending on the nature of the doping solution.

Doped homogeneous membrane presented lower water uptakes, especially membrane FAP. It was observed that the influence of the doping process on the water uptake was higher for the reinforcing AMX membrane. The doping process did not seem to affect the water uptake of FAP membrane. Although a definite trend with the type and concentration of electrolyte or alcohol was not either observed with any of the investigated homogeneous membranes, membrane AMX doped in presence of alcohol presented, in general, lower water uptakes with respect to the non doped membrane.

Table 6- Water uptake (WU), doping capacity (AU) Porosity (φ), FH interaction parameter (χ), parameter λ and volumetric fixed charge concentration ($\overline{X}$) for heterogeneous membrane PES doped in different electrolyte solutions.

Membrane PES		***WU* (%)**	***AU* (%)**	φ	χ	λ	$\overline{X}$ **(mol dm^{-3})**
			Water				
1M	**LiOH**	41	21	0.28	1.07	13	1.22
	NaOH	25	39	0.19	1.28	8	1.37
	KOH	44	22	0.30	1.04	14	1.20
2M	**LiOH**	41	29	0.28	1.07	13	1.23

	NaOH	30	32	0.22	1.20	9	1.33
	KOH	31	30	0.23	1.18	10	1.31
MeOH 1M							
1M	**LiOH**	31	34	0.22	1.19	9	1.32
	NaOH	33	32	0.24	1.16	10	1.30
	KOH	33	34	0.24	1.15	10	1.29
MeOH 2M							
1M	**LiOH**	30	34	0.22	1.20	9	1.32
	NaOH	39	25	0.27	1.09	12	1.25
	KOH	40	27	0.28	1.07	12	1.23
2M	**LiOH**	23	33	0.18	1.34	7	1.40
	NaOH	28	32	0.21	1.24	9	1.35
	KOH	29	32	0.21	1.22	9	1.34
EtOH 1M							
1M	**LiOH**	27	39	0.20	1.25	8	1.35
	NaOH	32	34	0.23	1.17	10	1.30
	KOH	30	38	0.22	1.20	9	1.32
EtOH 2M							
1M	**LiOH**	31	37	0.23	1.19	10	1.31
	NaOH	38	30	0.26	1.10	12	1.25
	KOH	28	40	0.21	1.24	9	1.35
2M	**LiOH**	24	31	0.19	1.31	7	1.39
	NaOH	34	29	0.24	1.15	10	1.29
	KOH	33	29	0.24	1.16	10	1.29
1-PrOH 1M							
1M	**LiOH**	25	37	0.19	1.29	8	1.37
	NaOH	25	45	0.19	1.30	8	1.38
	KOH	28	35	0.21	1.23	9	1.34

Table 7- Water uptake (*WU*), doping capacity (*AU*) Porosity (φ), FH interaction parameter (χ), parameter λ and volumetric fixed charge concentration ($\overline{X}$) for heterogeneous membrane PP doped in different electrolyte solutions.

Membrane PP		***WU* (%)**	***AU* (%)**	φ	χ	λ	$\overline{X}$ **(moldm^{-3})**
Water							
1M	**LiOH**	32	32	0.23	1.18	10	1.27
	NaOH	24	42	0.18	1.33	7	1.35
	KOH	31	34	0.22	1.20	10	1.28
2M	**LiOH**	32	34	0.23	1.18	10	1.27
	NaOH	23	45	0.17	1.36	7	1.37
	KOH	29	33	0.21	1.23	9	1.30
MeOH 1M							
1M	**LiOH**	20	50	0.15	1.43	6	1.40
	NaOH	23	44	0.18	1.34	7	1.36
	KOH	25	44	0.19	1.31	8	1.35
MeOH 2M							
1M	**LiOH**	21	50	0.16	1.41	6	1.39
	NaOH	32	33	0.23	1.18	10	1.27
	KOH	30	36	0.22	1.21	9	1.29
2M	**LiOH**	17	44	0.13	1.53	5	1.43
	NaOH	21	40	0.16	1.41	6	1.39
	KOH	22	45	0.17	1.37	7	1.37
EtOH 1M							
1M	**LiOH**	20	51	0.15	1.43	6	1.40
	NaOH	16	58	0.13	1.54	5	1.43
	KOH	27	37	0.20	1.27	8	1.32
EtOH 2M							
1M	**LiOH**	18	44	0.15	1.47	6	1.41
	NaOH	20	41	0.16	1.42	6	1.39
	KOH	30	31	0.22	1.21	9	1.29
2M	**LiOH**	16	47	0.13	1.57	5	1.44
	NaOH	23	43	0.18	1.34	7	1.36
	KOH	21	43	0.16	1.40	7	1.38
1-PrOH 1M							
1M	**LiOH**	19	51	0.15	1.46	6	1.41
	NaOH	16	59	0.13	1.56	5	1.44
	KOH	19	50	0.15	1.47	6	1.41

Table 8- Water uptake (*WU*), doping capacity (*AU*) Porosity (φ), FH interaction parameter (χ), parameter λ and volumetric fixed charge concentration ($\overline{X}$) for homogeneous membrane AMX doped in different electrolyte solutions.

Membrane AMX		***WU* (%)**	***AU* (%)**	φ	χ	λ	$\overline{X}$ **(mol dm^{-3})**
Water							
1M	**LiOH**	19	1	0.17	1.35	7	1.35
	NaOH	12	9	0.12	1.61	5	1.44
	KOH	16	3	0.15	1.45	6	1.39
2M	**LiOH**	14	4	0.13	1.55	5	1.42
	NaOH	9	12	0.09	1.81	3	1.49
	KOH	14	8	0.14	1.51	5	1.41
MeOH 1M							
1M	**LiOH**	15	3	0.14	1.47	6	1.40
	NaOH	15	4	0.14	1.51	5	1.41
	KOH	18	5	0.16	1.39	7	1.37
MeOH 2M							
1M	**LiOH**	13	4	0.12	1.60	5	1.44
	NaOH	12	5	0.11	1.63	4	1.45
	KOH	22	0	0.20	1.27	8	1.31
2M	**LiOH**	13	1	0.13	1.56	5	1.43
	NaOH	8	5	0.08	1.89	3	1.50
	KOH	10	3	0.10	1.75	4	1.48
EtOH 1M							
1M	**LiOH**	12	5	0.12	1.61	5	1.44
	NaOH	9	11	0.09	1.83	3	1.49
	KOH	14	8	0.13	1.53	5	1.42
EtOH 2M							
1M	**LiOH**	9	7	0.09	1.78	3	1.48
	NaOH	10	8	0.10	1.74	4	1.47
	KOH	10	11	0.10	1.74	4	1.47
2M	**LiOH**	11	1	0.10	1.71	4	1.47
	NaOH	13	4	0.12	1.59	5	1.43
	KOH	12	3	0.11	1.64	4	1.45
1-PrOH 1M							
1M	**LiOH**	12	4	0.12	1.63	4	1.45
	NaOH	2	16	0.03	2.83	1	1.59
	KOH	8	13	0.08	1.88	3	1.50

Table 9- Water uptake (*WU*), doping capacity (*AU*) Porosity (φ), FH interaction parameter (χ), parameter λ and volumetric fixed charge concentration ($\overline{X}$) for homogeneous membrane FAP doped in different electrolyte solutions.

Membrane FAP		***WU* (%)**	***AU* (%)**	φ	χ	λ	$\overline{X}$ **(mol dm^{-3})**
Water							
1M	**LiOH**	4	3	0.04	2.43	2	1.30
	NaOH	11	6	0.11	1.67	5	1.21
	KOH	2	7	0.03	2.83	1	1.32
2M	**LiOH**	9	4	0.09	1.79	4	1.23
	NaOH	8	3	0.09	1.84	4	1.24
	KOH	13	3	0.13	1.56	6	1.19
MeOH 1M							
1M	**LiOH**	8	2	0.09	1.84	4	1.24
	NaOH	8	3	0.09	1.83	4	1.24
	KOH	8	2	0.08	1.90	4	1.25
MeOH 2M							
1M	**LiOH**	3	3	0.03	2.63	1	1.31
	NaOH	10	1	0.10	1.70	5	1.22
	KOH	11	2	0.11	1.67	5	1.21
2M	**LiOH**	4	4	0.04	2.38	2	1.30
	NaOH	15	2	0.15	1.45	7	1.16
	KOH	6	0	0.06	2.09	3	1.27
EtOH 1M							
1M	**LiOH**	14	3	0.14	1.50	7	1.17
	NaOH	8	0	0.09	1.85	4	1.24
	KOH	10	1	0.10	1.71	5	1.22
EtOH 2M							
1M	**LiOH**	9	0	0.10	1.76	4	1.23
	NaOH	9	0	0.09	1.79	4	1.23
	KOH	9	1	0.09	1.78	4	1.23
2M	**LiOH**	12	3	0.12	1.60	6	1.20
	NaOH	13	0	0.13	1.54	6	1.18
	KOH	14	0	0.13	1.52	6	1.18
1-PrOH 1M							
1M	**LiOH**	5	6	0.05	2.25	2	1.29
	NaOH	8	10	0.08	1.90	4	1.25
	KOH	7	7	0.07	1.99	3	1.26

Although, in general, no significant trend was found between the type of electrolyte used for doping the FAP membrane and its water uptake, larger values of water uptake were observed in the case of NaOH in water and in 2M MeOH solution. This behavior does not seem to be related to the membrane doping capacity. It could be related to the membrane expansion properties in presence of hydroxide. As it will be shown in the next Section, this membrane presents, in general, a larger area expansion in presence of NaOH, indicating that the electrolyte nature may affect the membrane tensile strength .

When membranes were compared with respect to the doping capacity, higher values were observed for heterogeneous membranes. Membrane PP presented the highest doping capacity. For these membranes, an opposite tendency between doping and water uptake seems to be observed, so that at higher doping, lower water uptake. Homogeneous membranes presented a low doping capacity, especially non reinforcing FAP membrane which presented for some solutions a null doping capacity.

In general, a clearly defined trend with type and concentration of electrolyte and alcohol was not observed neither for membrane doping capacity nor the water uptake. Figure 2 shows the maximum and minimum values obtained for both water uptake and doping capacity for each membrane. With heterogeneous membranes, the maximum values for water uptakes were found with membranes doped in water. As it can be seen, the largest water uptake value was observed with membrane PES, corresponding with the membrane doped with KOH 1M in water. For this type of membranes, the minimum value corresponded with the membrane doped in presence of ethanol. Homogeneous membranes presented maximum values when they were doped in presence of methanol. For both homogeneous membranes, the water uptake minimum value was observed for membranes doped with KOH 1M in water. Regarding the doping capacity, also heterogeneous membranes presented the maximum values, corresponding with membranes doped with NaOH 1M in 1-PrOH 1M. Homogenous membranes also presented the maximum values when they were doped in presence of 1-PrOH 1M. The doping capacity was null for homogeneous membrane in different situations, mainly in presence of EtOH and MeOH.

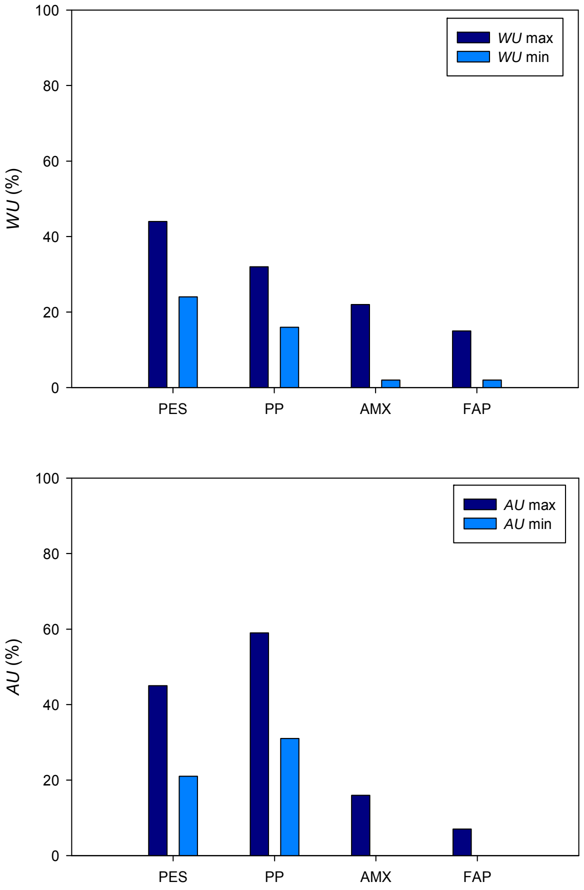

Fig. 2- Maximum and minimum values for water uptake (*WU*) and doping capacity (*AU*) for the investigated membranes.

As a high liquid uptake will lead to a higher ionic conductivity of the membrane in low-temperature fuel cells [16], it is expected a better behaviour of doped heterogeneous membranes in relation to the electric conductivity.

By using Eqs. (5) and (6), the membrane porosity and the FH interaction parameter can be estimated for all the investigated membrane systems. The results obtained for each membrane system are also shown in Tables 6 to 9.

Larger porosities were observed for heterogeneous membranes as expected from the results obtained for water uptakes. When comparing both heterogeneous membranes, membrane PES, with higher water uptake, showed higher porosity under the same conditions. The two homogeneous membranes presented similar low porosities in agreement with their higher density and lower water uptake. Regarding to the influence of the doping solvent nature, heterogeneous and homogeneous membranes presented, in general, lower porosities in presence of alcohol, but without defined trend with the type and concentration of alcohol. Neither a defined influence of the salt was observed, although a slight tendency to decrease with increasing salt concentration was observed for heterogeneous membranes.

The heterogeneous membranes showed larger water affinity. The presence of alcohol in the doping solution makes the FH parameters increases and so the membrane affinity decreases. The influence of the doping salt in the FH parameter depends on the alcohol. With all the membranes, for aqueous doping solutions, higher FH parameters were observed with NaOH, presenting LiOH and KOH similar values. In presence of alcohol, homogeneous and heterogeneous membranes presented different behavior depending on the alcohol type and on the salt and alcohol concentrations. In general, higher values were observed with LiOH.

The influence of the doping process on the membrane fixed charge concentration was investigated. The $\overline{X}$ values estimated for the doped membrane under different conditions are also shown in Tables 6-9. This parameter is of the great importance due to it greatly influences on the membrane selectivity. In heterogeneous membranes, the doping process makes the volumetric charge fixed concentration increases with respect to the non doped membrane, being the increase higher for PP membrane. For these membranes, in general, higher values of $\overline{X}$ are obtained when membranes were doped in presence of alcohol, although no definite trend was observed. Homogeneous membranes, however, showed different behaviors. A low increase of the fixed charge concentration was observed for reinforced AMX membrane, but a decrease was observed for FAP membrane. Neither of them presented a significant influence on the presence of alcohol in the doping solution.

3.3. Membranes in alkaline solutions.

3.3.1. Swelling properties

Swelling properties of the membranes in alkaline media were also investigated. The stability was checked in a similar way than for non-doped membranes. Fig. 3 shows the stable values obtained for the liquid content, S, and the surface expansion, E_A, of the membranes in presence of different concentration of alkaline hydroxides (LiOH, NaOH and KOH) in water and mixtures of water and alcohol (MeOH, EtOH and 1-PrOH) with diverse concentrations of alcohol. Fig. 3 also shows the values obtained in the absence of alkaline hydroxide to compare.

As general result, it can be noted the great influence of the alkaline medium in the swelling properties, as well as the different behaviour between homogeneous and heterogeneous membranes. In general, heterogeneous membranes presented higher liquid contents, with values near 100%, observing an increase in the liquid content in alkaline media with respect to the value obtained with the corresponding non electrolyte solution. Membrane PES presented the largest influence of the alkaline media in the solvent uptake. For this membrane, solvent uptake can increase up to more than 30% in presence of hydroxide.

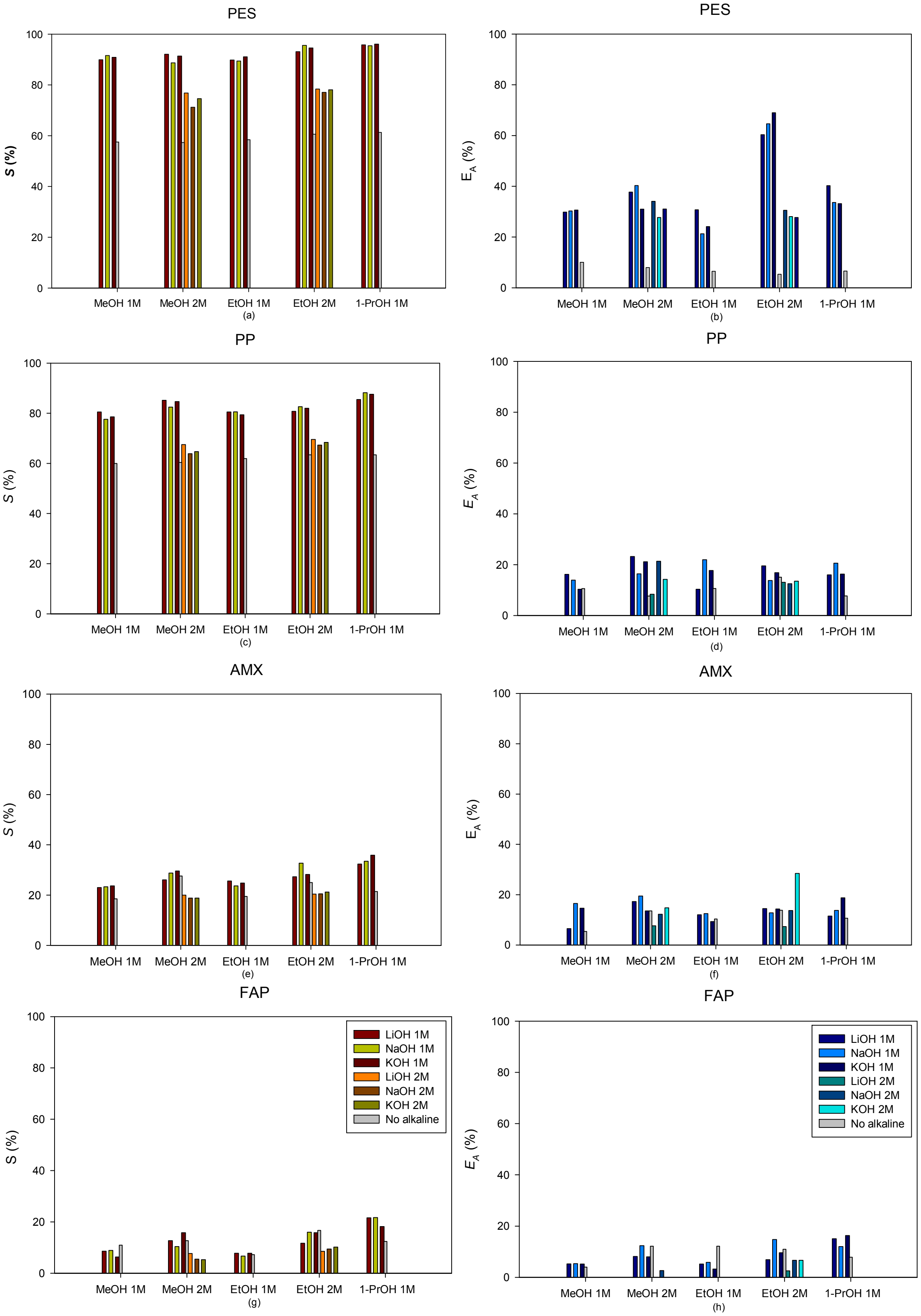

Fig. 3- Solvent uptake and area expansion for the investigated membranes in different alkaline solutions.

For homogeneous membranes, the presence of electrolyte slightly increased solvent uptake at low electrolyte concentration, but the opposite trend was observed at higher electrolyte concentration. However no definitely trend was observed with the type of alkaline hydroxide used.

For all the membrane systems, an increase of the electrolyte concentrations caused a decrease on the solvent uptake. When the membrane is soaked in an alkaline solution, alkali-doped free volume may be formed which can favours the liquid absorption. When the hydroxide concentration increases, the solution viscosity increases causing the ionic transport resistance increases. A similar behaviour has been observed in the ionic conductivity of anion exchange membranes in presence of NaOH [16, 36] and the competition between the favourable effect of increasing the ionic concentration and the observed effect of the increased viscosity in the alkali-doped free volumes of the membrane results in an optimal hydroxide concentration.

Concerning the surface expansion, it was in general favoured by the presence of hydroxide in the case of the heterogeneous membranes. Heterogeneous PES membrane, with higher solvent uptakes, also presented the higher expansion, mainly with EtOH 2M and low hydroxide concentration. However, for homogeneous membranes the presence of hydroxide in the solution had in general a less effect on the membrane surface expansion and no clear trend was observed.

In summary, the results presented in Fig. 3 show that in hydroxide media anion heterogeneous membranes are more hydrophilic than anion homogeneous membranes, as for cation exchange membranes. In general, the higher the membrane density, the lower water content and the larger the relative influence of the presence and type of electrolyte. A low solvent content favours the possible interaction between counter-ion and the membrane fixed charge groups [37]. On the other hand, the presence of the free alkali in the membrane matrix would lead to the reduced intermolecular forces as a result of the increased separation distance. Therefore, the tensile strength of the membranes would be much smaller than in absence of doping.

3.2.2. Fixed charge concentration

The membrane fixed charge concentration has been estimated, in the case of aqueous solution, for all the hydroxides and concentrations. The densities of aqueous hydroxide solutions used in Eq. (7) were taken from data in references [38-41]. The obtained results are shown in Fig. 4.

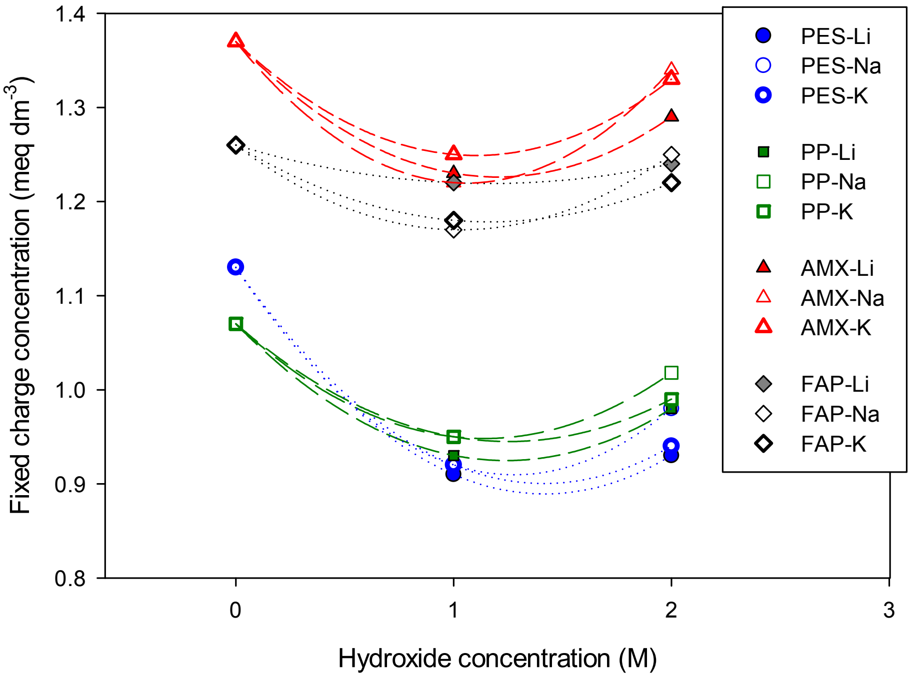

Fig. 4-Fixed charge concentration for the investigated membranes in hydroxide aqueous solutions. Lines are only visual guides.

As it can be observed, the presence of hydroxide in the solution causes the membrane fixed charge concentration decreases a low electrolyte concentration, being the observed decrease higher for heterogeneous membranes. However, when the hydroxide concentration increased, an increase of this parameter was observed. This result was similar for all the investigated membranes and it would indicate that a minimum hydroxide concentration would be necessary to increase the charge fixed concentration of the membrane by adding a hydroxide. Homogeneous membranes presented larger charge fixed concentrations, due to their lower uptake, independently of the presence and nature of the hydroxide. In general, the influence of the type of hydroxide is small for all the membranes, although it tends to increase when the hydroxide concentration increases. The homogeneous membrane AMX presented the higher fixed charge concentration.

4. Conclusions

Liquid uptake is an important endowment of ion-exchange membranes and has significant effect on separation phenomena, dimensional as well as mechanical properties. The dissociation of charged functional groups could be promoted by the presence of water molecules inside the membrane matrix and so it is very important for the transport of ions. As water is also known to assist the mass transport of alcohol and oxygen in a fuel cell, the solvent uptake measurement could serve as a quantitative measure of membrane performance for a direct alcohol fuel cell application as well. In this work, four commercial polymeric anion-exchange membranes –two heterogeneous and two homogeneous- were compared in terms of swelling properties. The effect of an alkaline medium is analyzed. It is experimentally found that: (i) The membrane structure strongly affects the membrane swelling properties. (ii) Liquid uptake and expansion are higher with water-alcohol mixtures than with pure liquids for heterogeneous membranes. For homogeneous membranes, the influence of the type of solvent is small. (iii) Regardless of the alkali-metal doping, heterogeneous membranes present higher liquid uptakes and dimensional changes. (iv) The effect of an added hydroxide in the solvent on the membrane water uptake is strong. In general, the higher the membrane density, the lower water content and the larger the relative influence of the presence and type of electrolyte. Concerning the surface expansion, it was in general favoured by the presence of hydroxide in the case of heterogeneous membranes and with a less effect on the homogeneous membranes. As a high liquid uptake will lead to a higher ionic conductivity of the membrane in low-temperature fuel cells, these results suggest a better behaviour of heterogeneous membrane in relation to the electric conductivity.

Acknowledgments

Financial support of this work by Banco de Santander and Universidad Complutense de Madrid within the framework of Project 910358 UCM Research Group-GR3/14 is gratefully acknowledged.

REFERENCES

[1] Dyer K. Fuel cells for portable applications. J Power Sources. 2002;106: 31-34.

[2] Antolini E, Gonzalez ER. Alkaline direct alcohol fuel cells. J Power Sources 2010;195:3431-3450.

[3] García-Nieto D, Barragán VM. A comparative study of the electro-osmotic behavior of cation and anion exchange membranes in alcohol-water media. Electrochim Acta 2015;184:166-176.

[4] Matsuoka K, Iriyama Y, Abe T, Matsuoka M, Ogumi Z. Alkaline direct alcohol fuel cells using an anion exchange membrane. J Power Sources 2005;150:27-31.

[5] Yu EH, Krewer U, Scott K. Principles and Materials Aspects of direct alkaline alcohol fuel cells. Energies 2010;3:1499-1528.

[6] Merle G, Wessling M, Nijmeijer K. Anion exchange membranes for alkaline fuel cells: A review. J Membrane Sci 2011;377:1-35.

[7] Cheng J, He G, Zhang F. A mini-review on anion exchange membranes for fuel cell applications: stability issue and addressing strategies. Int J Hydrogen Energ 2015;40:7348-7360.

[8] Agel E, Bouet J, Fauvarque JF. Characterization and use of anionic membranes for alkaline fuel cells. J Power Sources 2001;101:267-274.

[9] Kreuer KD. Ion conducting membranes for fuel cells and other electrochemical devices. Chem Mater 2014;26:361-380.

[10] Carmo M, Frizt DL, Merge J, Stolen D. A comprehensive review on PEM water electrolysis. Int J Hydrogen Energ 2013;38:4901-4934.

[11] Veerman J, Jong RM, Saakes M, Metz SJ, Harmsen GJ. Reverse electrodialysis: Comparison of six commercial membrane pairs on the themodynamic efficiency and power density. J Membrane Sci 2009;343:7-15.

[12] Balster J, Pünt I, Stamatialis DF, Lammers K, Verver AB, Wessling M. Electrochemical acidification of milk by whey desalination. J Membrane Sci 2007;303:213-220.

[13] Souilah O, Akretche DE, Amara M. Water reuse of an industrial effluent by mean of electrodeionisation. Desalination 2004;167:49-54.

[14] Karas F, Hnát J, Paidar M, Schauer J, Bouzek K. Determination of the ion-exchange capacity of anion-elective membranes. Int J Hydrogen Energ 2014;39:5054-5062.

[15] Li YS, Zhao TS, Yang WW. Measurements of water uptake and transport properties in anion-exchange membranes. Int J Hydrogen Energ 2010;35:5656-5665.

[16] An L, Zhao TS, Wu QX, Zeng L. Comparison of different types of membranes in alkaline direct ethanol fuel cells. Int J Hydrogen Energ 2012:37:14536-14542.

[17] Wang X, McClure JP, Fedkiw PS. Transport properties of proton- and hydroxide-exchange membranes for fuel cells. Electrochim Acta 2012;79:126-132.

[18] Han KW, Ko KH, Abu-Hakmeh K, Bae C, Sohn YJ, Jang SS. Molecular dynamics simulation study of a polysulfone-based anion exchange membrane in comparison with the proton exchange membrane. J Phys Chem C 2014;118:12577-12587.

[19] Gao TZ, Kandel BS, Oh SJ. Properties of poly(vynil alcohol)-based composite membranes for direct methanol fuel cell applications. J Chin Chem Soc-Taip 2007;54:1485-1494.

[20] Verjulio RW, Santander J, Sabaté N, Esquivel JP, Torres-Herrero N, Habrioux A, Alonso-Vante N. Fabrication and evaluation of a passive alkaline membrane micro direct methanol fuel cell. Int J Hydrogen Energ 2014:39:5406-5413.

[21] http://www.tokuyama-a.com/ion_exchange.php; 2003 [accessed 12.03.16].

[22] http://www.ralex.eu/Membrany/Uvod.aspx; 2003 [accessed 12.03.16].

[23] http://www.eetcorp.com/lts/membraneproperties.pdf; 2003 [accessed 12.03.16].

[24] http://www.fumatech.com/NR/rdonlyres/EEC52087-35BF-4F88-A682-C2306172FC93/0/5667_Fumatech_fumasep_Einzelseiten.pdf; 2003 [accessed 12.03.16].

[25] González B, Calvar N, Gómez E, Dominguez A. Density, dynamic viscosity, and derived properties of binary mixtures of methanol or ethanol with water, ethyl acetate, and methyl acetate at T = 293.15, 298.15, and 303.15 K. J Chem Thermodyn 2007:39:1578-1588.

[26] Pang FM, Seng CE, Teng TT, Ibrahim MH. Densities and viscosities of aqueous solutions of 1-propanol and 2-propanol at temperatures from 293.15 K to 333.15 K. J Mol Liq 2007:136:71-78.

[27] Strathmann H. Ion-Exchange Membrane Separation Processes. In: Membrane Science and Technology Series, Amsterdam: Elsevier; 2004.

[28] Li YS, Zhao TS, Yang WW. Measurements of water uptake and transport properties in anion-exchange membranes. Int J Hydrogen Energ 2010;35:5656-5665.

[29] Zeng L, Zhao TS, An L, Zhao G, Yan XH. Physicochemical properties of alkaline doped polybenzimidazole membranes for anion exchange membrane fuel cells. J Membrane Sci 2015;493:340-348.

[30] Randová A, Hovorka S, Izák P, Bartovská L. Swelling of Nafion in methanol-water-inorganic salt ternary mixtures. J Electroanal Chem 2008;616:117-121.

[31] Morris DR, Sun X. Water-sorption and transport properties of Nafion 117. J Appl Polym Sci 1993;50:1445-1442.

[32] Godino MP, Barragán VM, Villaluenga JPG, Izquierdo-Gil MP, Ruiz-Bauzá C, Seoane B. Liquid transport through sulfonated cation-exchange membranes for different water-alcohol solutions. Chem Ing 2010;162:643-648.

[33] Barragán VM, Muñoz S. Influence of a Microwave irradiation on the swelling and permeation properties of a Nafion membrane. J Membrane Sep Technol 2015;4:32-39.

[34] Mizutani Y. Structure of ion exchange membranes. J Membrane Sci 1990;49:212-144.

[35] Lehmani A, Turq P, Périé M, Périé J, Simonin J-P. Ion transport in Nafion 117 membrane. J Electroanal Chem 1997;428:81-89.

[36] Agel E, Bouet J, Fauvarque JF. Characterization and use of anionic membranes for alkaline fuel cells. J Power Sources 2001;101:267-274.

[37] Barragán VM, Pérez-Haro MJ. Correlations between water uptake and effective fixed charge concentration at high univalent electrolyte concentrations in sulfonated polymer cation-exchange membranes with different morphology. Electrochim Acta 2011;56:8630-8637.

[38] http://www.solvaychemicals.com; 2003 [accessed 12.03.16].

[39] Akerlof G, Bender P. The density of aqueous solution of potassium hydroxide. J Am Chem Soc 1941;63:1085-1088.

[40] Sipos PM, Hefter G, May PM. Viscosities and densities of highly concentrated aqueous MOH solutions (M+= Na+, K+, Li+ Cs+, (CH$_3$)4N+) at 25ºC. J Chem Eng Data 2000;45:613-617.

[41] Corti HR, Fernández Prini R, Svarc F. Densities and partial molar volumes of aqueous solutions of lithium, sodium and potassium hydroxides up to 250ºC. J Solution Chem 1990;19:793-809.

Figure caption

Fig.1- Typical chemistry structure (a) of a quaternary ammonium-type anion-exchange membrane (Neosepta AMX membrane), (b) of a fluorinated-type anion-exchange membrane.

Fig.2- Maximum and minimum values for water uptake (*WU*) and doping capacity (*AU*) for the investigated membranes.

Fig.3- Solvent uptake and area expansion for the investigated membranes in different alkaline solutions.

Fig.4- Fixed charge concentration for the investigated membranes in hydroxide aqueous solutions. Lines are only visual guides.