

Short communication

# Water and methanol transport in Nafion membranes with different cationic forms

## 1. Alkali monovalent cations

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Received 21 December 2005; received in revised form 2 February 2006; accepted 4 February 2006

Available online 22 March 2006

### Abstract

The mass flux originated when two methanol–water solutions of different methanol concentration are separated by a Nafion 117 membrane in acid ( $H^+$ ) and different alkali metal forms ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ) have been measured, as a function of the methanol concentration difference. From the experimental results, the methanol and water permeabilities have been estimated for the different forms of the membrane. The results show that the cationic form of the membrane strongly influences on the methanol and water permeabilities with respect to the values corresponding to its acid form. Moreover, this influence is different for water and methanol depending on the substituted cation. This strong influence of the cationic form of the membrane on the methanol and water permeabilities could be important in relation to the development of new membranes to decrease the methanol crossover in direct methanol fuel cells.

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*Keywords:* Nafion; Membrane cationic form; Water–methanol solutions; Permeability; Direct methanol fuel cells

### 1. Introduction

In a direct methanol fuel cell (DMFC), methanol is oxidized at the anode, in the presence of water, to form protons, electrons and carbon dioxide. The electrons move through an external circuit, and protons are transported through a polymer electrolyte membrane. Any unreacted methanol, however, can also diffuse from the anode to the cathode through the polymer electrolyte membrane. This methanol transfer is known as crossover, and it causes depolarization losses at the cathode and conversion losses in fuel, affecting the performance at the direct methanol fuel cell. The phenomena caused by methanol crossover in the DMFCs are well summarized in the literature [1–7].

Poly (perfluorosulphonic) acid ionomer (Nafion) is extensively used as polymer electrolyte membrane in DMFCs. The

properties that make the Nafion membrane indispensable are the combination of good water uptake, ion-exchange capacity, proton conductivity, low gas permeability, and an excellent electrochemical stability. Otherwise, the high methanol permeability and dehydration at high temperatures make necessary to look for alternative membranes that are relatively impermeable to methanol. One of the ways to find alternative membranes focuses on modifying Nafion membranes [8–11]. Along this line, some authors have observed changes in the behavior of the membrane when it is doped with different cations [12–22]. But most of the studies focus on membrane equilibrium and transport properties referred to aqueous media. Nevertheless, the study of the influence of the cationic form of the membrane on water and methanol transport processes involved in a direct methanol fuel cell would be very interesting for developing new membranes.

The aim of this work is to analyze the influence of the cationic form of a Nafion membrane on its water and methanol permeabilities. With this purpose, the methanol and water transport originated by a methanol concentration difference have been studied in Nafion membranes substituted by different monovalent cations.

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## 2. Experimental

### 2.1. Materials

A commercial membrane Nafion 117 with a nominal equivalent weight of  $1100 \text{ g eq}^{-1}$  was used in this study. The thickness, maximum water uptake and ion-exchange capacity provided by the manufacturer for this membrane are 0.183 mm, 35% and  $1.13 \text{ kmol m}^{-3}$ , respectively. In this work Nafion membranes were used as received without any previous treatment. Nafion 117 as received was treated first with 0.25 M HCl for its complete conversion. Metal ionic forms were generated from the acid form by immersing the membrane in a solution containing 0.25 M of an appropriate solution (LiCl, NaCl, KCl, RbCl, CsCl) during 48 h for counter-ion exchange at ambient temperature, followed by washing with deionized water and drying the superficial water with filter paper [17]. The active area of the membrane was  $25.3 \times 10^{-4} \text{ m}^2$ .

Pure pro-analysis grade methanol and salts (Merck) and deionized bidistilled pure water were used in the present study.

### 2.2. Apparatus

The experimental device used in the present study is similar to one reported elsewhere [13,23]. The membrane cell consisted of two independent chambers made of PTFE of approximately  $10^{-4} \text{ m}^3$  of volume separated by the membrane. Each chamber was provided with three orifices communicating to the exterior. In both chambers a temperature probe was introduced in one of the orifices, so the temperature was measured at a distance of 0.02 m from the membrane. The other two orifices were used as solution inlet and outlet.

Two glass reservoirs of about  $10^{-3} \text{ m}^3$  of capacity were used to contain the circulating solutions in both chambers. Each reservoir was provided with three orifices. Two orifices were used as solution inlet and outlet. In the third orifice, in order to avoid any pressure difference built-up between the reservoirs, one L-shaped capillary tube was introduced in each reservoir, and they were kept at the same height.

Each reservoir had a jacket made of glass, where water maintained at constant temperature of  $25^\circ\text{C}$  was circulating by means of a Techne TU-16D thermostat. Moreover, one of the reservoirs was placed over a mass balance (Sartorius BL3100 model), which permitted to measure the mass change in the reservoir as a function of time. The accuracy in the mass measurement was  $\pm 10^{-4} \text{ kg}$ .

The temperature measurement in the cell was conducted by using an electronic device (Jenco 1671 model) with an accuracy of  $\pm 0.1^\circ\text{C}$ .

Measurements were performed by using pure water in one chamber, and pure methanol or mixtures of water and methanol with a methanol content of 20, 40, 60 and 80% (w/w) in the other chamber. The methanol–water solutions were previously degassed in order to prevent the bubble formation during the measurement process.

The solutions were made to circulate between the reservoirs and the cell by means of a peristaltic pump (Masterflex L/S

model. Cole-Parmer). The circulation velocity of the solutions was  $300 \text{ mL min}^{-1}$ .

### 2.3. Methods

At the beginning of the experiments, the solutions were placed in the reservoirs. In one of the reservoir pure water was placed, while a methanol–water mixture was placed in the other reservoir. When the temperature of the solutions placed in each reservoir reached the selected value of  $25^\circ\text{C}$ , the solutions were made to circulate through the cell, and the mass change was measured as a function of time in the reservoir placed over the mass balance. This reservoir was always the one contained the diluted solution (water initially).

The initial solution densities in both reservoir, and the concentrated solution density as a function of time were measured at  $20^\circ\text{C}$  by means of a AP Paar Density Meter, model DMA58, with a accuracy of  $\pm 10^{-2} \text{ kg m}^{-3}$ . Using the data for the density dependence with methanol concentration (wt. %) found in the literature at  $20^\circ\text{C}$  [24], it is obtained that the methanol–water solution density as a function of the methanol concentration in the mixture can be fitted to a polynomial. Using this fit, it is possible, from the value of the density, to obtain the corresponding value of the methanol concentration.

## 3. Results and discussion

### 3.1. Determination of the total mass flux and the concentration change

The mass change in the diluted chamber, when the membrane separated two methanol–water solutions of different methanol concentration, was measured as a function of time. The measurements were performed with different methanol concentration differences between both chambers, and with different cationic forms of the membrane. Fig. 1 shows, as an example, the results corresponding to the  $\text{Na}^+$ -form Nafion membrane. As it can be observed, after a period of time, a linear relationship was

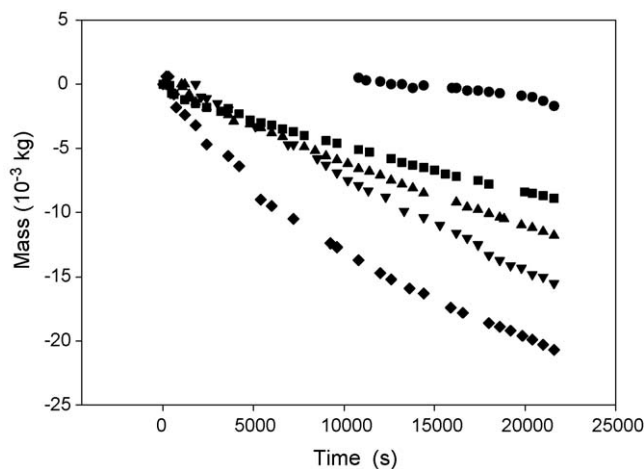


Fig. 1. Mass change in the diluted chamber as a function of time at different methanol concentration differences: (●) 20 wt.%; (■) 40 wt.%; (▲) 60 wt.%; (▼) 80 wt.%; (◆) 100 wt.%. The data correspond to the  $\text{Na}^+$ -form of the membrane.

Table 1

Total mass flux,  $\beta$ , as a function of the initial methanol concentration difference (wt.% MeOH) for the different cationic forms of the membrane

MeOH (wt.%)	$\beta$ ( $10^{-7}$ kg s $^{-1}$ )					
	H	Li	Na	K	Rb	Cs
20	-0.93 ( $\pm 0.05$ )	-2.13 ( $\pm 0.07$ )	1.60 ( $\pm 0.10$ )	0.87 ( $\pm 0.17$ )	-0.11 ( $\pm 0.04$ )	$\approx 0$
40	-3.77 ( $\pm 0.10$ )	-2.93 ( $\pm 0.07$ )	3.97 ( $\pm 0.07$ )	2.33 ( $\pm 0.05$ )	-1.15 ( $\pm 0.08$ )	$\approx 0$
60	-3.57 ( $\pm 0.07$ )	-3.63 ( $\pm 0.13$ )	5.40 ( $\pm 0.07$ )	2.50 ( $\pm 0.05$ )	-0.44 ( $\pm 0.04$ )	$\approx 0$
80	-3.60 ( $\pm 0.05$ )	-3.43 ( $\pm 0.08$ )	7.63 ( $\pm 0.07$ )	1.87 ( $\pm 0.03$ )	-0.55 ( $\pm 0.04$ )	$\approx 0$
100	-5.27 ( $\pm 0.05$ )	-6.37 ( $\pm 0.17$ )	9.6 ( $\pm 0.4$ )	3.27 ( $\pm 0.10$ )	0.54 ( $\pm 0.04$ )	$\approx 0$

found, indicating that pseudosteady–steady conditions prevailed during the experiment after an initial transient. For each experimental situation, the results have been fitted to a straight line. In all cases, this linear dependence permits to obtain the total mass flux,  $\beta$ , from the slope of the corresponding straight line. Interestingly, it was found that the direction of the total mass flow depends on the cationic form of the membrane. Table 1 shows the values obtained for  $\beta$  as a function of the initial concentration of methanol in the concentrated chamber for the different cationic forms of the Nafion membrane. The values are referred to the concentrated chamber, in such a way that a negative value of  $\beta$  indicates that the total mass flux was observed from the concentrated to the diluted chamber. As it can be observed in Table 1, the sign of the total mass flux depends on the cationic form of the membrane. It is worth mentioning that in the case of the Cs $^{+}$ -form of the membrane, there was no mass change.

During each experiment, besides of the total mass flux, the methanol concentration in the concentrated chamber was also determined as a function of time. Fig. 2 shows, as an example, the results obtained for the acid form of the membrane. It is observed that the higher concentration difference between both chambers, the higher methanol concentration change in the concentrated chamber. A linear dependence between methanol concentration and time was also found in all the cases. The results were analogous for all the cationic forms of the membrane. Again, the

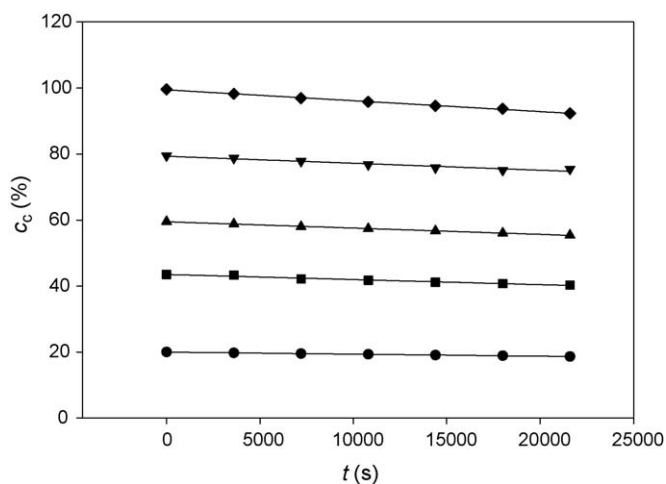


Fig. 2. Methanol concentration in the concentrated chamber as a function of time at different methanol concentration differences: (●) 20 wt.%; (■) 40 wt.%; (▲) 60 wt.%; (▼) 80 wt.%; (◆) 100 wt.%. The data correspond to the acid form of the membrane.

linear dependence permitted to obtain the concentration change velocity,  $\alpha$ , from the slope of the corresponding straight line. Fig. 3 shows the value the  $\alpha$  obtained as a function of the atomic number,  $N$ , of the exchanged ion at different initial values of the methanol concentration in the concentrated chamber. The dotted lines are only a visual guide. As it was expected, for a given cationic form of the membrane, the higher the concentration difference, the higher the parameter  $\alpha$ . Moreover, a strong dependence of the parameter  $\alpha$  on the form of the membrane is observed. While the value of  $\alpha$  increases in the case of Li and Na, with respect to the value corresponding to the acid form of the membrane, for cation with higher atomic number, the value of  $\alpha$  decreases. It is found a maximum in the curves showing  $\alpha$  as a function of the atomic number of the substituted cation. This influence is qualitatively similar for all the concentration differences, but quantitatively, the higher the concentration difference, the higher effect.

### 3.2. Determination of the methanol and water fluxes

The total mass flux  $\beta$  was due to two contributions, a methanol flux, for diffusion, and a water flux, for osmosis, both originated as a consequence of the methanol concentration difference established between two sides of the membrane. It is interesting to know the flux of each component in the mixture. Thus, the individual fluxes of methanol and water through the membrane were

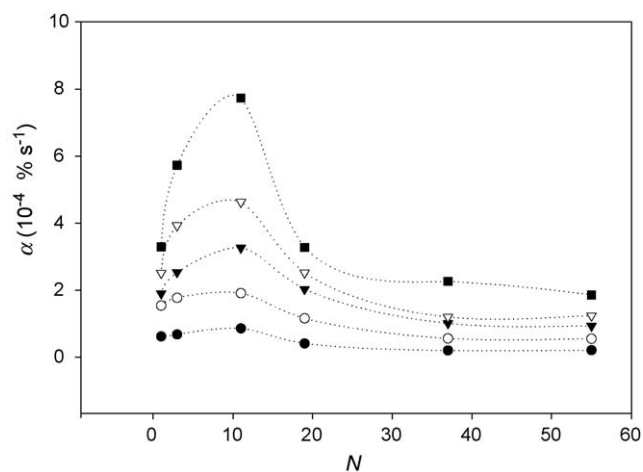


Fig. 3. Concentration change velocity,  $\alpha$ , as a function of the atomic number of the substituted cation for different methanol concentration differences: (●) 20 wt.%; (○) 40 wt.%; (▼) 60 wt.%; (▽) 80 wt.%; (■) 100 wt.%. Dotted lines are only visual guides.

estimated by using data of  $\alpha$ ,  $\beta$ , and the initial mass in the concentrated chamber.

The methanol,  $J_{\text{MeOH}}$ , and water,  $J_{\text{H}_2\text{O}}$ , fluxes through the membrane are given by the following expressions:

$$J_{\text{MeOH}} = \frac{1}{A} \frac{dm_c^m}{dt} = -\frac{1}{A} \frac{dm_d^m}{dt} \quad (1)$$

$$J_{\text{H}_2\text{O}} = \frac{1}{A} \frac{dm_c^w}{dt} = -\frac{1}{A} \frac{dm_d^w}{dt} \quad (2)$$

where  $m_c^m$  and  $m_d^m$  are the methanol masses in the concentrated and diluted chambers, respectively, and  $m_c^w$  and  $m_d^w$  are, respectively, the water masses in the concentrated and the diluted chambers. Moreover, the methanol concentration,  $c_c$ , expressed in wt.%, in the concentrated chamber is given by:

$$c_c = \frac{m_c^m}{m_c} \times 100 \quad (3)$$

where  $m_c$  is the total mass in the concentrated chamber. Taking into account the previous experimental results for the total mass flux and the time change of the concentration in the concentrated chamber, a linear dependence as a function of time can be assumed for  $c_c$  and  $m_c$  during the time of the experiment, i.e.,

$$c_c = c_c^0 + \alpha t \quad (4)$$

$$m_c = m_c^0 + \beta t \quad (5)$$

where  $c_c^0$  and  $m_c^0$  are the initial concentration and the initial mass, respectively, in the concentrated chamber, and  $\alpha$  and  $\beta$  are the coefficients that determine, respectively, the concentration and total mass changes with time. Thus, if Eqs. (1)–(3) are considered, the methanol mass in the concentrated chamber as a function of time can be expressed as:

$$m_c^m = \frac{1}{100}(c_c^0 + \alpha t)(m_c^0 + \beta t). \quad (6)$$

The total mass in the concentrated chamber is the sum of the methanol and water masses in this chamber, i.e.,

$$m_c = m_c^m + m_c^w, \quad (7)$$

thus, from Eqs. (6) and (7), the water mass in the concentrated chamber as a function of time is given by the following equation:

$$m_c^w = \frac{1}{100}(100 - c_c^0 - \alpha t)(m_c^0 + \beta t) \quad (8)$$

Then, taking into account Eqs. (1), (2), (6) and (7), methanol and water fluxes at short times, can be described by the following equations:

$$J_{\text{MeOH}} = \frac{1}{100A}[(c_c^0\beta + \alpha m_c^0) + (2\alpha\beta)t] \quad (9)$$

$$J_{\text{H}_2\text{O}} = \frac{1}{100A}[(100\beta - c_c^0\beta - \alpha m_c^0) - (2\beta\alpha)t] \quad (10)$$

Finally, the methanol,  $J_{\text{MeOH}}^0$ , and water,  $J_{\text{H}_2\text{O}}^0$ , fluxes originated by a given initial methanol concentration difference,  $\Delta c_0$ ,

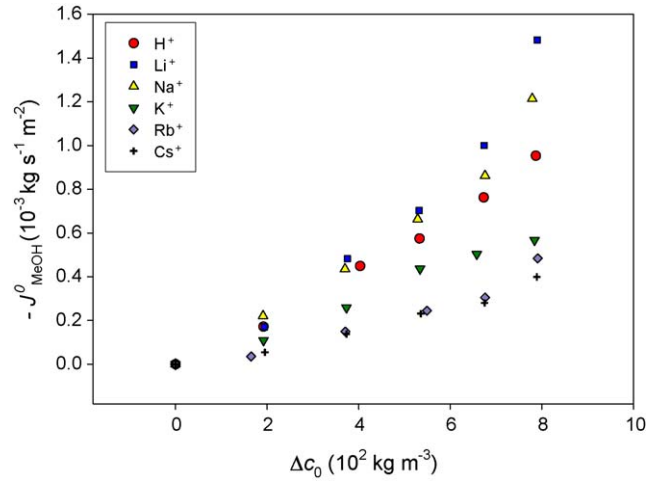


Fig. 4. Methanol flux as a function of the initial methanol concentration difference for different cationic forms of the membrane.

can be estimated from the extrapolation at zero time of  $J_{\text{MeOH}}$  and  $J_{\text{H}_2\text{O}}$ , thus

$$J_{\text{MeOH}}^0 = \frac{1}{100A}(c_c^0\beta + \alpha m_c^0) \quad (11)$$

$$J_{\text{H}_2\text{O}}^0 = \frac{1}{100A}(100\beta - c_c^0\beta - \alpha m_c^0) \quad (12)$$

Figs. 4 and 5 show, respectively, the methanol and water fluxes estimated from Eqs. (11) and (12) as a function of the initial methanol difference concentration  $\Delta c_0$ . The negative value of the methanol flux indicates that the methanol flux is originated from the concentrated to the diluted chamber, as can be expected in a diffusion process. In contrast, a positive flux of water was found, indicating that the flow of water was originated in the opposite direction, as can be expected in an osmotic process. It should be pointed out that depending on the relative value of the methanol and water fluxes, the total flux will be observed in one direction or in the opposite one, depending on the relative value of the methanol and water fluxes. This would explain the data

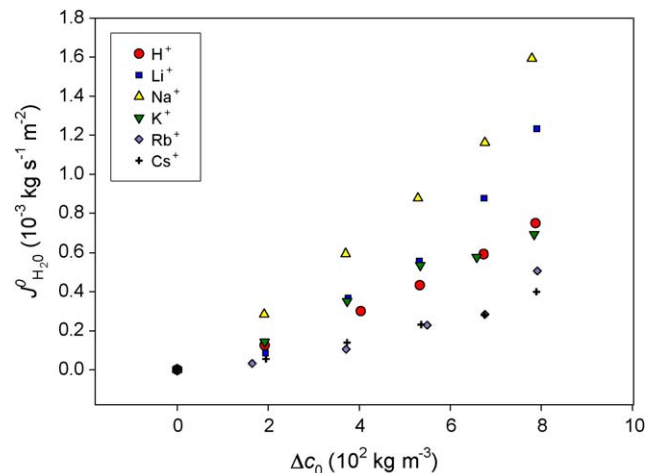


Fig. 5. Water flux as a function of the initial methanol concentration difference for different cationic forms of the membrane.

given in Table 1. For example, in the case of the Cs<sup>+</sup>-form membrane, the zero value of  $\beta$ , indicates that methanol and water fluxes are equal. On the other hand, the general trend is that the interchanged masses of methanol and water increase with the methanol concentration difference. In addition, the influence of the cationic form of the membrane on the individual fluxes is different. Thus, in the case of the methanol flux, it is observed that the higher the atomic number of the exchanged cation, the lower the methanol flux for the metal forms of the membrane. Comparing with the results obtained for the methanol flux in the acid form of the membranes, it is observed that the Li<sup>+</sup>- and Na<sup>+</sup>-forms of the membrane favor the methanol transport, while that lower methanol fluxes are found for the rest of the cations. The behavior of the water flux with the cationic form of the membrane is similar to the previously described for the methanol flux, with the exception of the Li<sup>+</sup>-form of the membrane, which exhibits a lower water flux than the Na<sup>+</sup>-form. Then, in this case, non monotonous trend is observed with varying the atomic number of the substituted cation. Finally, no significant influence of the methanol concentration difference on the ratio of methanol and water fluxes has been observed for each form of the membrane.

### 3.3. Estimation of the methanol and water permeabilities

The analysis of Figs. 4 and 5 shows, in almost the whole range of concentration, a linear relationship between flux and methanol concentration difference, as it is predicted by the Fick's law. Nevertheless, a positive deviation from the linear behavior at the high  $\Delta c_0$  values is observed, especially for the membrane forms with lower atomic number ions. The experimental data were fitted to a first-order polynomial, and the methanol and water permeabilities were estimated from the slope of the corresponding straight lines. The values obtained for the permeability are plotted in Fig. 6 as a function of the atomic number of the substitute exchange ion of the membrane. The dotted lines are only a visual guide. It is found that the water and methanol permeabilities are of the order of  $10^{-6} \text{ m s}^{-1}$  for the acid form of

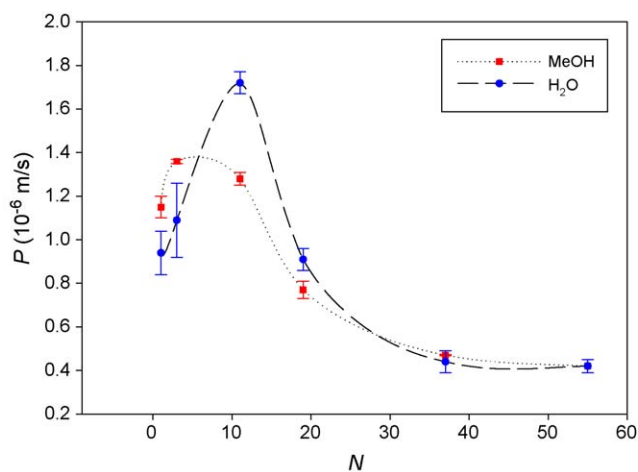


Fig. 6. Methanol and water permeabilities as a function of the atomic number of the substituted cation. The lines are only visual guides.

the Nafion membrane, which is in agreement with the results obtained by other authors [25,26].

Fig. 6 shows that, in general, the permeability decreases with the atomic number of the substitute ion for the metal form membrane, with the exception of the water permeability in the Na<sup>+</sup>-form membrane, whose value is relatively high. It is also found that the water and methanol permeability in the acid form of the membrane is lower than that in its Li<sup>+</sup>- and Na<sup>+</sup>-forms, and higher than that in its K<sup>+</sup>-, Rb<sup>+</sup>- and Cs<sup>+</sup>-forms. In addition, it can be observed that the cationic form of the membrane affects not only the absolute values of the methanol and water permeabilities, but also their relative values. Thus, in the acid H<sup>+</sup>-form of the membrane, the methanol permeability is higher than the water permeability. This fact is also found in the case of the Li<sup>+</sup>-form of the membrane, but the opposite is observed for the rest of the cationic forms of the membrane. Moreover, the difference between methanol and water permeabilities becomes lower when the atomic number of the cation increases, and for the Cs<sup>+</sup>-form of the membrane both values are practically the same. The Na<sup>+</sup>-form of the membrane shows a higher difference between the methanol and water permeabilities.

The influence of the cationic form of the membrane on its transport properties may be explained on the basis of the alterations produced by the presence of the cation in the membrane microstructure, which affects the hydrophilic domains through methanol and water diffuse primarily. Different works suggest that the physical structure of Nafion 117 membrane in H<sup>+</sup> form may be quite different from the Nafion 117 with other monovalent counterions [14,18,19]. Different authors have found a decrease of the water uptake of Nafion membranes doped with alkali monovalent cations when the atomic number of the substituted cation increases [14–16,20,22]. In general, for water sorption the following trend was observed: H<sup>+</sup> > Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> > Cs<sup>+</sup> [14,16]. In the case of methanol sorption, the sequence is similar with the exception of H<sup>+</sup> and Li<sup>+</sup>. Suresh et al. [14] found that for methanol sorption, both H<sup>+</sup> and Li<sup>+</sup> forms of the membrane exhibited similar sorption amount, and the sequence found by Nandan et al. [16] for the methanol sorption was Li<sup>+</sup> > H<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> > Cs<sup>+</sup>. These authors also found a great difference between the solvent uptakes with Na<sup>+</sup> and K<sup>+</sup>, and that the difference between both uptakes becomes smaller at large size cations. The decrease of the water and methanol permeabilities for cations with higher atomic number observed in the present study is in accordance with the behavior reported by other authors. Thus, this fact may be related to the drastic reduction of solvent uptake of the membrane when the cation size increases. The high value of the water permeability for the Na<sup>+</sup> form membrane is probably due to the influence of the water uptake on the membrane thickness. Nandan et al. [16] found that the ratio of a Nafion 117 membrane thickness in methanol to that of water is 1.34 for Na<sup>+</sup>-form of the membrane, higher than for the other cationic forms.

These results show that the methanol and water transport of the membrane can be altered by doping the membrane with an appropriate cation, which may be very interesting in order to reduce methanol crossover in direct methanol fuel cells.



#### 4. Conclusions

From the experimental results of the mass flux and of the methanol concentration change velocity, originated when two methanol–water solutions of different methanol concentration are separated by a Nafion membrane, the methanol and water permeabilities have been estimated for different cationic forms of the membrane. The obtained values are of the order of  $10^{-6} \text{ m s}^{-1}$ , in agreement with the results obtained by other authors.

The data show that the membrane cationic form strongly affects the methanol and water transport properties of the membrane. As a general trend, it is obtained that both, the individual methanol and water permeabilities decrease when the cation size increases. This decrease observed in both permeabilities for cations with higher atomic numbers may be related to the drastic reduction of the membrane solvent uptake when the cation size increases.

The results show that, in order to reduce the methanol crossover in direct methanol fuel cells, the methanol transport through the membrane can be altered by doping the membrane with an appropriate cation.

#### Acknowledgement

Financial support from the University Complutense of Madrid under Project 052PR13273 is gratefully acknowledged.

#### References

- [1] A. Heinzel, V.M. Barragán, *J. Power Sources* 84 (1999) 70–74.
- [2] J. Cruickshank, K. Scott, *J. Power Sources* 70 (1998) 40–47.
- [3] J. Zhang, Y. Wang, *Fuel Cells* 4 (2004) 1–2.
- [4] M. Shen, K. Scott, *J. Power Sources* 148 (2005) 24–31.
- [5] V.M. Barragán, A. Heinzel, *J. Power Sources* 104 (2002) 66–72.
- [6] J. Kallo, J. Kamera, W. Lehnert, R. Von Helmolt, *J. Power Sources* 127 (2004) 181–186.
- [7] V. Gogel, T. Frey, Z. Yonsgsheng, K.A. Friedrich, L. Jörnsen, J. Garche, *J. Power Sources* 127 (2004) 172–180.
- [8] H.L. Tang, M. Pan, S.P. Jiang, R.Z. Yuan, *Mater. Lett.* 59 (2005) 3766–3770.
- [9] P. Dimitrova, K.A. Friedrich, U. Stimming, B. Vogt, *Solid State Ionics* 150 (2002) 115–122.
- [10] W.C. Choi, J.D. Kim, S.I. Woo, *J. Power Sources* 96 (2001) 411–414.
- [11] H. Lin, T.L. Yu, L. Huang, L. Chen, K. Shen, G. Jung, *J. Power Sources* 150 (2005) 11–19.
- [12] V. Tricoli, *J. Electrochem. Soc.* 145 (1998) 3798–3801.
- [13] V.M. Barragán, C. Ruiz-Bauzá, J.P.G. Villaluenga, B. Seoane, *J. Power Sources* 130 (2004) 22–29.
- [14] G. Suresh, X.M. Scindia, A.K. Pandey, A. Goswami, *J. Membr. Sci.* 250 (2005) 39–45.
- [15] N.H. Jalani, R. Datta, *J. Membr. Sci.* 264 (2005) 167–175.
- [16] D. Nandan, H. Mohan, R.M. Iyer, *J. Membr. Sci.* 71 (1992) 69–80.
- [17] L.G. Lage, P.G. Delgado, Y. Kawano, *Eur. Polym. J.* 40 (2004) 1309–1316.
- [18] T. Okada, H. Satou, M. Okuno, M. Yuasa, *J. Phys. Chem. B* 106 (2002) 1267–1273.
- [19] A. Goswami, A. Acharya, A.K. Pandey, *J. Phys. Chem. B* 105 (2001) 9196–9201.
- [20] M. Legras, Y. Hirata, Q.T. Nguyen, D. Langevin, M. Métayer, *Desalination* 147 (2002) 351–357.
- [21] M. Kameche, C. Innocent, F. Xu, G. Pourcelly, Z. Derriche, *Desalination* 168 (2004) 319–327.
- [22] S. Koter, P. Piotrowski, J. Kerres, *J. Membr. Sci.* 153 (1999) 83–90.
- [23] J.P.G. Villaluenga, B. Seoane, V.M. Barragán, C. Ruiz-Bauzá, *J. Membr. Sci.* 274 (2006) 116–122.
- [24] J. D'Ans, H. Surawsky, C. Synowietz, Densities of liquid systems and their capacities, in: *Numerical Data and Functional Relationships in Science and Technology. Group IV. Macroscopic and Technical Properties of Matter*, vol. 1, Springer, New York, 1977.
- [25] H.A. Every, M.A. Hickner, J.E. McGrath, T.A. Zawodzinski, *J. Membr. Sci.* 250 (2005) 183–188.
- [26] P.S. Kauranen, E. Skou, *J. Appl. Electrochem.* 26 (1996) 909–917.