

# A review of the state-of-the-art of the methanol crossover in direct methanol fuel cells

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## Abstract

Direct (oxidation) methanol fuel cells (DMFCs) are attractive for several applications, however, there are several barriers which must be overcome before they can become an alternative to internal combustion engines. At present, methanol crossover from the anode to the cathode appears to be the major limitation. This work shows the information on the influence of methanol crossover in DMFC and on the effort to get a more methanol-impermeably polymer electrolyte found in the literature. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Direct (oxidation) methanol fuel cells (DMFCs) are attractive for several applications in view of their lower weight and volume compared with indirect fuel cells. In this kind of fuel cells, solid polymers have been shown as an attractive alternative to the traditional liquid electrolytes. Nafion<sup>®</sup> perfluorosulfonic acid polymers are the most commonly used fuel cell membranes. Although it would be desirable methanol could be spontaneously oxidised at the cathode, however, a methanol transport across the membrane has been observed. It causes depolarisation losses at the cathode and conversion losses in terms of lost fuel.

In order to improve the performance of the DMFC, it is necessary to eliminate or, at least, to reduce the loss of fuel across the cell, usually termed “methanol crossover”. In this sense, the membrane technology is one of the alternatives for trying to solve this problem.

The present work focuses on showing the studies found in the literature about “methanol crossover” and its influence on the performance of DMFCs, mainly from the point of view of the solid polymer electrolyte.

## 2. Methanol transfer through Nafion<sup>®</sup> membranes

In the most of the work found in literature, Nafion<sup>®</sup> membranes are used as solid polymer electrolyte in DMFCs. The works which study directly the properties of the methanol transfer through the membrane are scarce and, usually, the study of the methanol crossover is carried out from its influence on the performance of the fuel cell.

As the most important result, it must be said that methanol readily transports across perfluorosulfonic acid membranes. Verbrugge [1], by using a radioactive tracer method, measured the methanol diffusivity of Nafion equilibrated with sulfuric acid at room temperature. By means of comparing experimental results and theoretical results from a mathematical model capable of simulating quantitatively methanol-transport experiments, estimated the effective diffusion coefficient to be  $1.15 \times 10^{-5} \text{ cm}^2/\text{s}$  at 25°C for a Nafion<sup>®</sup> 117. Kauranen and Skou [2] developed a method for the measurement of the permeability of methanol in proton exchange membranes equilibrated with a supporting liquid electrolyte at elevated temperatures. From the time responses of anodic peak currents on two working electrodes, they estimated that the permeability of methanol for a Nafion<sup>®</sup> 117 perfluorosulfate membrane, at 60°C, was  $4.9 \times 10^{-6} \text{ cm}^2/\text{s}$ , and the activation energy was about 12 kJ/mol, increasing the permeability of methanol with increasing temperature with an Arrhenius

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dependence. An increase of the crossover rate with temperature was also found by Narayanan et al. [3] for Nafion® 117 membranes. These authors measured the methanol crossover rates by estimating the carbon dioxide content of the cathode exit stream. Crossover rates were reported as an equivalent current density of methanol oxidation.

Narayanan et al. [3] also studied the dependence of the crossover rate on the current density, finding it to decrease with increasing current density due to an increased utilisation of methanol at high current densities.

The influence of the helium pressure on the permeate side of the membrane on the permeation rates for water, methanol and water–methanol mixture through Nafion® 117 was studied by Cruickshank and Scott [4]. In all cases, the experimental permeation rates were of the order of  $10^{-6}$  mol/cm<sup>2</sup> s and they decreased as the helium pressure increased. From a simple model to describe the permeation of methanol from the anode to the cathode in DMFC, they obtained that the effective diffusion coefficient was of the order of  $10^{-5}$  cm<sup>2</sup>/s for Nafion® 117 membranes and at temperature values between 70 and 96°C and estimated the electroosmotic drag coefficient in 0.164 MeOH/H<sup>+</sup>.

The influence of the thickness of the membrane has been studied by Jung et al. [5] by using three kinds of Nafion membranes, 117, 115 and 112 at constant temperature and testing the methanol concentration remaining in the drain water coming from the cathode by gas chromatography. The results obtained, used pure oxygen as cathode fed, showed that the weight percent of methanol remaining in the drain water coming from the cathode outlet was three times higher for the membrane electrode assembly using the Nafion 112 membrane than for the membrane electrode assembly using the Nafion 117 membrane. As a result the methanol permeation rates through the membrane are expected to be higher in the thinner membranes. This result agrees with those found by Narayanan et al. [3] who observed that the membrane thickness had a significant impact on crossover. They observed that increasing the thickness from 5 to 14 mils caused the crossover to reduce by about 40–50%. This can be attributed to the reduction of methanol crossover with increasing mass transfer resistance in the membrane.

Studying the crossover rate in DMFC with Nafion membranes of different equivalent weight, these authors observed that high equivalent weight Nafion types exhibit lower methanol permeability, probably due to the increase of the transfer resistance in the membrane.

### 3. Effect of the methanol crossover in the DMFC performance using Nafion® membranes

Due to the impact of methanol crossover on the performance of the DMFC, its effects have been studied in the literature under various operating conditions. Next, a re-

view of the influence of the different operating parameters are shown.

#### 3.1. Influence of the concentration of methanol

If methanol crossover is a cause of a reduction in cell voltage it would be expected that a higher concentration of methanol in the feed to the anode would decrease the cell voltage as a result of potentially higher rates of transport through the membrane. In fact, it has been observed that the open circuit voltages decrease with increasing methanol concentration [5]. This lower performance of the cell at higher methanol concentrations is attributed to the fuel crossover phenomenon [3,4,6–8]. It was found that the cathode electrode performance is significantly lowered at higher methanol concentration [9]. However, at high current densities, it is observed a lower performance of the cell at lower concentration of methanol. This is probably due to the concentration polarisation effects. It is necessary, thus, to find the optimal concentration under the operating conditions of the fuel cell.

#### 3.2. Influence of the pressure

The experimental works found have shown that there is a significant effect of increasing the O<sub>2</sub>/air pressure on cell performance which cannot be predicted from thermodynamic or kinetic behaviour. Scott and Taama [8] and Scott et al. [10] developed a model of a DMFC based on a solid polymer electrolyte membrane which took into account the methanol crossover. This model could explain the cell voltages were significantly lower and decreased when the oxygen pressure was reduced to a range of practical operating current densities up to approximately 350–400 mA/cm<sup>2</sup>. This influence was also observed by Cruickshank and Scott [4] who stated that pressurising the oxygen reduced the crossover of methanol, leading to higher cell voltages. Narayanan et al. [3] observed that the effect of pressure on the voltage is more significant at low rates than high flow rates. Likewise, the effect of flow rate was less significant at higher pressures. The impact of working at ambient pressure on the cell voltage was the greatest at low flow rates and low temperatures.

#### 3.3. Influence of the temperature

Jung et al. [5] found, using Nafion 117 and 2.5 M methanol, an increase of the performance of the cell when the operating temperature increased. They attributed this higher performance to the combined effects of a reduction of ohmic resistance and polarisation. In fact, the ionic conductivity of Nafion membranes, increases with increasing temperature [3]. This result agrees with those obtained by Surampudi et al. [6] with Nafion 117 membranes and 2 M methanol fuel cell in the range of 30–90°C, and with the results presented in [7–9], where it is found that a

difference in the operation temperature makes a significant difference in the cell performance. Thus, in spite of the fact that the increase of the temperature increases the methanol crossover, as was previously mentioned [2,3], the results found in the literature seem to indicate that the increase of the temperature improves the cell performance. For this reason, some authors have studied the possibilities of vapour-feed DMFCs [11].

### 3.4. Influence of the thickness and equivalent weight of the membrane

As it was previously said, methanol crossover decreases when the thickness of the membrane increases. This fact agrees with the results found by Jung et al. [5] and Narayanan et al. [3] about the increase of the open circuit voltages with increasing membrane thickness. However, this trend changes at the highest current densities because membrane resistance to transport phenomena became dominant. This fact is related to the reduction of resistance of charge transfer from the anode side to the cathode side and the reduction of concentration polarisation in the polymer with the decreasing of membrane thickness. Thus, the electrical performance of fuel cell with membranes of various thicknesses shows that the performance trend is probably determined by the combined effects of ionic conductivity and fuel crossover. As a result at higher thicknesses, the ohmic resistance of the cell could be determining the cell voltage, although there would have been some enhancement of the cell voltage due to reduced crossover. Something similar occurs with the influence of the equivalent weight in the performance of the cell. Electrical performance studies [3] on various membranes of different equivalent weights indicated a small reduction in voltage and increase in slope with increasing membrane equivalent weight due to high equivalent weight Nafion-types exhibit lower methanol permeability, as was previously said. But at highest density currents, the electrical performance of a DMFC may be decrease when the equivalent weight of the membrane decreases.

In Table 1, a summary of the general influence of the different studied operating parameters on the crossover

methanol and in the fuel cell performance is shown for Nafion® membrane DMFCs.

### 3.5. Influence of the catalyst morphology

The cell performance is also limited by the anode catalyst activity and the cathode exhibits a degree of methanol tolerance. Optimisation of the electrode structure leading to higher catalyst utilisation, will also contribute to increased cell performance. One of the major chemical problems of the methanol crossover is its impact on the cathode operation and system efficiency.

Narayanan et al. [3] by measuring individual electrode potentials, showed that improvement to the anode catalyst activity can greatly enhance the performance at 60°C in the low to medium current density range, while improvement in the air electrode performance is also required at higher current densities.

Increased catalyst loading has been demonstrated to improve the performance of direct methanol cells [12]. At present the most active catalysts are based on platinum–ruthenium materials [13]. A recent work of Küver and Vielstich [7] shows that a good performance has been obtained employing 29% PtRu on Norit BRX thus giving a total noble metal loading of only 2.3 mg/cm<sup>2</sup> or 1.6 mg Pt/cm<sup>2</sup>.

## 4. Comparative study of the influence of methanol crossover in different types of membranes

As the fuel crossover causes considerable cell voltage losses in the DMFC different approaches to minimise or eliminate methanol crossover have been carried out from different points of view. The electrooxidation of methanol only occurs at a useful rate in the presence of platinum or a platinum-based electrocatalyst. This had to an intensive search for alternative materials which can oxidise methanol at lower potential and, in particular, for additional secondary materials that might combine with platinum to promote the process. For his reason, considerable efforts have recently been made in the DMFC electrocatalysts

Table 1

Influence of increasing different operating parameters in the methanol crossover and in the fuel cell performance

Parameter	Nafion® membranes		
	Methanol crossover	Cell performance	
		Low current density	Highest current density
Cell temperature	favourable	favourable	favourable
Cathode pressure	unfavourable	favourable	favourable
Feed concentration	favourable	unfavourable	favourable
Current density	unfavourable	unfavourable	unfavourable
Membrane thickness	unfavourable	favourable	unfavourable
Membrane equivalent weight	unfavourable	favourable	unfavourable

[7,12–19]. The performance of the DMFC would be improved considerably if a methanol-tolerant cathode existed. An alternative is the membrane technology trying to obtain a new methanol-impermeable polymer electrolyte [20–28].

Pu et al. [20] studied a composite electrolyte where a film of a methanol impermeable protonic conductor (MIPC), such as a metal hybrid [29], was sandwiched between proton permeable electronic insulators, such as Nafion. They studied different electrolyte systems where the proton permeable electronic insulator was Nafion 115 membrane and the metal hybrid was Pd, and the influence of interfaces modification with Pt via various techniques. The results obtained showed that the methanol crossover was smaller than in the Nafion polymer and that the higher performance was obtained with the system (N/Pt/Pd/Pt/N), where N is the Nafion 115 membrane, and by palladization of the Pd surface followed by platinumization using electrochemical methods common to the preparation of hydrogen reference electrodes.

Küver and Potje-Kamloth [21] showed new ways of electrochemical modification of conventional fuel cell materials for the purpose of reducing the system's methanol crossover. They studied the methanol crossover in substituted and crosslinked POP membranes (sulphonate-substituted polyoxiphenylenes) using differential electrochemical mass spectrometry. They compared the results obtained with those obtained with different commercial membranes such as Nafion 117 (Du Pont) or XUS (Dow Chemical). It was found that Nafion 117 was superior to XUS with respect to methanol permeation, and the superiority of POP membranes was evident and specially attractive in light of the fact that the thickness of Nafion and XUS membranes were 175 and 125  $\mu\text{m}$ , respectively, and the POP film was only 0.2 to 0.3  $\mu\text{m}$  thick. These authors also studied the influence of the crosslinking grade observing that a high crosslinking grade was superior in retaining the methanol.

Wainright et al. [22] studied the conductivity, water content and methanol vapour permeability of the phosphoric acid-doped polybenzimidazole (PBI). From the results obtained about the sorption of methanol in the electrolyte and about methanol diffusivity, they estimated the permeability of these membranes on  $15 \times 10^{-16} \text{ m}^3 \text{ (STP)m/m}^2 \text{ s Pa}$ . Experimental results confirmed this low methanol crossover in a PEM fuel cell employing a doped polybenzimidazole membrane with a crossover current on the order of 10 mA/cm<sup>2</sup>.

Weng et al. [23] studied the electroosmotic coefficient of water and methanol in this polymer at elevated temperatures, showing that both of them must be near zero.

Wang et al. [24] and Wasmus et al. [25] showed a method for determining the methanol crossover rate within a working device in order to study the influence of certain fuel cell operating conditions, such as the current density on the methanol crossover. Using this method with a

Table 2

Influence of increasing different operating parameters in the methanol crossover and in the fuel cell performance

Parameter	Acid-doped PBI membranes	
	Methanol crossover	Cell performance
Cell temperature	unfavourable	favourable
Anode pressure	favourable	unfavourable
Feed concentration	favourable	unfavourable
Current density	favourable	unfavourable

DMFC using acid-doped PBI membranes, they observed that the methanol crossover rate increased with an increasing current due to methanol drag. Thus, although the drag coefficient was very small, in agreement with the results obtained in Ref. [23], the effect of the methanol drag at high current density may become significant.

Compared to a Nafion membrane, acid doped PBI membranes show several advantages. They have good protonic conductivity and mechanical flexibility at elevated temperature, and exhibit excellent oxidative and thermal stability [26]. They have an almost zero electroosmotic drag number and low methanol gas permeability. Thus, several investigations have been carried out to study the influence of the different operating parameters in the methanol crossover through acid-doped PBI membranes.

Wainright et al. [27] and Wang et al. [28] studied the methanol crossover and the performance of a DMFC employing PBI membranes. They observed that methanol crossover rate increased with a decrease in the water/methanol ratio in the anode feed stream. This result agrees with the results found in the literature for Nafion<sup>®</sup> membranes. These authors, however, found that methanol crossover increased with increasing current density and decreased when temperature increased. The influence of increasing of different operating parameters in the methanol crossover and in the performance of DMFCs using acid doped PBI membranes are shown in Table 2.

Tricoli [30], by investigating the influence of doping poly(perfluorosulfonated acid) membranes with cesium to several degrees on the methanol permeability at room temperature, found that the membrane permeability can be drastically reduced by an appropriate doping cesium ions.

## 5. Conclusions

Methanol crossover from the anode to the cathode appears to be a major limitation at present for DMFCs to become a commercially viable alternative.

Although Nafion<sup>®</sup> membranes are the most usually used as solid polymer electrolyte in DMFCs, the investigations found in literature shows that methanol readily transports across perfluorosulfonic acid membranes and, in order to minimise the effects of methanol crossover, alternative membrane materials have been sought. Acid doped

PBI membranes seems to have a lower methanol permeability than Nafion<sup>®</sup> membranes.

An alternative to new membrane technology, in order to minimise the effect of the methanol crossover, is to improve the activity of methanol electrooxidation catalysts.

The studies about the influence of the different operating parameters on the methanol crossover show that high temperatures and high cathode pressures make methanol crossover decrease and improve the cell performance. In relation to the influence of the concentration of methanol, in spite of increasing the methanol concentration the crossover increases, it is necessary to take into account the polarisation phenomena at the lowest concentration and so, to find the optimal concentration under the operating conditions of the fuel cell.

The experimental results found in the literature show that methanol crossover decreases when the thickness and the equivalent weight of the membrane increase. However, due to the increase of the membrane resistance with the increasing of these parameters, the performance of fuel cell with membranes or various thicknesses and equivalent weights is determined by the combined effects of ionic conductivity and fuel crossover.

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### References

- [1] M.W. Verbrugge, *J. Electrochem. Soc.* 136 (1989) 417.
- [2] P.S. Kauranen, E. Skou, *J. Appl. Electrochem.* 26 (1996) 909.
- [3] S.R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M. Smart, T.I. Valdez, S. Surampudi, G. Halpert, *Annu. Battery Conf. Appl. Adv.* 11 (1996) 113.
- [4] J. Cruickshank, K. Scott, *J. Power Sources* 70 (1998) 40.
- [5] D.H. Jung, C.H. Lee, C.S. Kim, D.R. Shin, *J. Power Sources* 71 (1998) 169.
- [6] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K. Surya Prakash, G.A. Olah, *J. Power Sources* 47 (1994) 377.
- [7] A. Küver, W. Vielstich, *J. Power Sources* 74 (1998) 211.
- [8] K. Scott, W. Taama, *J. Appl. Electrochem.* 28 (1998) 289.
- [9] M.K. Ravikumar, A.K. Shukla, *J. Electrochem. Soc.* 143 (1996) 2601.
- [10] K. Scott, W. Taama, J. Cruickshank, *J. Power Sources* 65 (1997) 159.
- [11] A.K. Shukla, P.A. Christensen, A. Hamnett, M.P. Hogarth, *J. Power Sources* 55 (1995) 87.
- [12] S.R. Narayanan, G. Halpert, W. Chun, B. Jeffries-Nakamura, T.I. Valdez, H. Frank, S. Surampudi, *Proc. Power Sources Conf.* 3764 (1996) 96.
- [13] M.P. Hogarth, G.A. Hards, *Platinum Met. Rev.* 40 (1996) 150.
- [14] A. Küver, I. Vogel, W. Vielstich, *J. Power Sources* 52 (1994) 77.
- [15] J.A. Kosek, C.C. Cropley, A.B. LaConti, *Electrochem. Soc. Proc.* 96 (1996) 322.
- [16] S. Gupta, D. Tryk, S.K. Zecevic, W. Aldred, D. Guo, R.F. Savinell, *J. Appl. Electrochem.* 28 (1998) 673.
- [17] L. Li, P. Cong, R. Viswanathan, F. Qinbai, L. Renxuan, E.S. Smotkin, *Electrochim. Acta* 43 (1998) 3657.
- [18] A.S. Arico, P. Creti, P.L. Antonucci, J. Cho, H. Kim, V. Antonucci, *Electrochim. Acta* 43 (1998) 3719.
- [19] F. Gloaguen, J.-M. Le'ger, C. Lamy, *J. Appl. Electrochem.* 27 (1997) 1052.
- [20] C. Pu, W. Huang, K.L. Ley, E.S. Smotkin, *J. Electrochem. Soc.* 142 (1995) L119.
- [21] A. Küver, K. Potje-Kamloth, *Electrochim. Acta* 43 (1998) 2527.
- [22] J.S. Wainright, J.-T. Wang, D. Weng, R.F. Savinell, M. Litt, *J. Electrochem. Soc.* 142 (1995) L121.
- [23] D. Weng, J.S. Wainright, U. Landau, R.F. Savinell, *J. Electrochem. Soc.* 143 (1996) 1260.
- [24] J.-T. Wang, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 143 (1996) 1233.
- [25] S. Wasmus, J.T. Wang, R.F. Savinell, *J. Electrochem. Soc.* 142 (1995) 3825.
- [26] S.R. Samms, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 143 (1996) 1225.
- [27] J.S. Wainright, J. Wang, R.F. Savinell, *Proc. Intersoc. Energy Convers. Eng. Conf.* 31 (1996) 1107.
- [28] J.-T. Wang, J.S. Wainright, R.F. Savinell, M. Litt, *J. Appl. Electrochem.* 26 (1996) 751.
- [29] V.N. Verbetsky, S.P. Malysenko, S.V. Mitrokhin, V.V. Solovei, Y.F. Shmal'ko, *Int. J. Hydrogen Energy* 23 (1998) 1165.
- [30] V. Tricoli, *J. Electrochem. Soc.* 145 (1998) 3798.