# **Proton-Conducting Polymers with Reduced Methanol Permeation**

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**ABSTRACT:** The permeability of Nafion<sup>®</sup>117 and some types of acid-base and covalently crosslinked blend membranes to methanol was investigated. The methanol crossover was measured as a function of time using a gas chromatograph with a flame ionization detector. In comparison to Nafion, the investigated acid-base and covalently crosslinked blend membranes show a significant lower permeation rate to methanol. Additionally, another method to reduce the methanol permeability is presented. In this concept a thin barrier layer is plasma polymerized on Nafion 117 membranes. It is shown that a plasma polymer layer with a thickness of 0.3  $\mu$ m reduces the permeability to methanol by an order of magnitude. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 67–73, 1999

**Key words:** methanol permeation; proton-conducting polymers; Nafion; acid-base blend membranes; barrier layers; plasma polymer films

## **INTRODUCTION**

The permeation of methanol through ionomer membranes has received a large interest recently, because these membranes can be used as ionicconducting polymers in direct methanol fuel cells (DMFC).<sup>1,2</sup> Most DMFCs operate with perfluorosulfonate ionomer membranes, such as Nafion<sup>®</sup>. In comparison to a conventional  $H_2/O_2$  fuel cell the DMFCs have several advantages including compactness of size, lower weight, and the absence of any fuel processing system. One major problem of DMFCs is the loss of fuel due to the permeation of methanol across the Nafion membrane. This large methanol permeability of Nafion not only reduces fuel efficiency but also increases the overpotential of the cathode, thus lowering cell performance.<sup>3</sup>

In this article we report work on new ionomer membranes with a significant lower methanol crossover. These ionomer membranes include PSU (Polysulfone Udel®)-sulfinate/PSU-sulfonate blend membranes covalently crosslinked via sulfinate-alkylation with  $\alpha,\omega$ -diiodobutane,<sup>4</sup> and different types of acid-base blend membranes: 1. PSU-SO<sub>3</sub>H/PSU-NH<sub>2</sub>, 2. PEEK (Poly(etheretherketone) PEEK Victrex®)-SO<sub>3</sub>H/PSU-NH<sub>2</sub>, 3. PEEK-SO<sub>3</sub>H/PBI (Polybenzimidazole Celazole®), and 4. PSU-SO<sub>3</sub>H/PBI.<sup>5–7</sup> The polymers combined to acid-base blend membranes are shown in Figure 1.

The acid-base blends show specific interaction between the blend components. These are hydrogen bridges and formation of salt pairs that are ionic crosslinks<sup>5-7</sup>

 $Polymer-SO_3H + Polymer-NH_2 \rightarrow$ 

 $Polymer-SO_{3}^{-} {}^{+}H_{3}N-Polymer \quad (1)$ 

By mixing a water-soluble sulfonated polymer with a basic polymer, water-insoluble blends can

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**Figure 1** Polymer components of the acid-base blend membranes.

be produced. The specific interaction between acidic and basic polymer prevents the acidic polymer component from being dissolved in water. Nafion is an uncrosslinked membrane, while the investigated blend membranes are covalently or ionically crosslinked. This leads, in comparison to Nafion, to a lower methanol permeability.

Additionally, we present results of an alternative approach to reduce the methanol permeability. In this concept, we use a plasma-processing technique to deposit a thin plasma polymerized film on Nafion membranes to improve their barrier properties. The membranes are exposed to a low-pressure plasma excited by microwaves. Gas mixtures of hexan ( $C_6H_{14}$ ) an hydrogen ( $H_2$ ) were used as monomers.

#### **EXPERIMENTAL**

#### **Permeation Measuring Device**

The permeability of methanol through the ionomer membranes was performed in the device shown in Figure 2. Recently, this experimental setup has been used for investigations concerning the permeability of toluene through polyethylene foils.<sup>8,9</sup>

The membranes were placed between the two compartments of the permeation cell. The upper part of the cell is filled with "pure" methanol. The methanol molecules permeate through the membrane into the opposite compartment of the permeation cell. There, a constant nitrogen  $(N_2)$  gas flow carries the methanol molecules to the flame ionization detector (FID) of a gas chromatograph. The FID is highly sensitive to methanol and other hydrocarbons, but not sensitive to N<sub>2</sub>. The resulting signal of the FID is continously recorded. The permeation measurements were performed with a  $N_2$  flow rate of 60 sccm, adjusted by a mass flow controller (MFC). A possible leakage in the nitrogen supply or the permeation cell was controlled by a mass flow meter (MFM) at the outlet of the cell.

Because the diffusion coefficient and the permeability strongly depend on the temperature, the permeation cell was placed in a temperature bath with constant temperature. The permeation



Figure 2 Permeation measuring device.



pumping unit

Figure 3 Schematic diagram of the plasma device.

measurements of the membranes were performed at a temperature of 40°C. Both compartments of the permeation cell were sealed by O-rings. The active area was 86 mm<sup>2</sup>. The upper compartment contains a further O-ring for sealing the membranes against the water of the temperature bath.

### **Plasma Reactor**

In this study, we apply a plasma-processing technique to deposit a thin layer on Nafion membranes to reduce the crossover of methanol.

The plasma device, called Duo-Plasmaline<sup>®</sup> is shown in Figure 3.<sup>10</sup> The plasma is excited by microwaves at a frequency of f = 2.45 GHz. The Duo-Plasmaline operates in a stainless steel chamber with a diameter of 80 cm and a height of 80 cm. The microwaves are fed into the reactor from both ends of a quartz tube with an inner copper rod. The inside of the tube is at atmospheric pressure, while the outside is at low pressure. The plasma ignites outside the tube at the low pressure side. An axially homogeneous plasma is formed with a length up to the diameter of the vacuum chamber. This linearly extended plasma source is well suited for many industrial applications. Details of the plasma generation mechanism is described elsewhere.<sup>11</sup>

The experiments were performed in gas mixtures of hexan ( $C_6H_{14}$ ) and hydrogen ( $H_2$ ). These gases were supplied to the plasma chamber by means of a gas inlet system, consisting of electronic flow meters. The gas flow rate is measured in the units of sccm. For example, a gas mixture ratio of 10:40 means a gas flow rate of 10 sccm hexan and 40 sccm hydrogen during the deposition process. A typical pressure for plasma deposition was 30 Pa. The microwave power of 2.4 kW  $(2 \cdot 1.2 \text{ kW})$  was modulated with an on-off pulse cycle of 8 to 6 ms. The modulation technique minimized thermal load of the membranes during the deposition process.

#### **Electric Resistance (Impedance Spectroscopy)**

The electric resistance of the membranes was determined with impedance spectroscopy (IM6 Impedance measurement system, Zahner elektrik) in two different plexiglass cells with gold-plated copper electrodes of 0.25 cm<sup>2</sup> electrode area. The impedance, where the phase angle between current and voltage was zero, was taken as the (ohmic) ion-exchange membrane resistance R<sup>H+</sup>. The membrane was mounted between two Nafion 117 membranes and then the stack, composed of Nafion-test membrane-Nafion, was pressed between the two electrodes. The measurements were performed in a 0.5 N HCl electrolyte solution at a temperature of 25°C. The membrane/electrode interface resistance was eliminated by first measuring the stack, followed by a measurement of the two Nafion membranes, and then subtracting the impedance of the Nafion membranes from the impedance of the stack.

#### Membrane Swelling

The membranes first were equilibrated in water at ambient temperature, and then the swollen membranes were weighted  $(m_{wet})$ . Subsequently, the membranes were dried in the drying oven at increased temperature (90°C) and weighted again  $(m_{dry})$ . Then the swelling degree was determined via following formula:

$$SW = ((m_{wet} - m_{drv})/m_{drv}) \times 100 \ (\%) \quad (2)$$

# **RESULTS AND DISCUSSION**

#### **Characteriziation of the Polymer Blends**

The characterization data of the different acidbase and covalently crosslinked blend membranes and of the Nafion membrane are gathered in Table I. Here, c.c. and i.c. means <u>covalently</u> and <u>ionically crosslinked</u>. IEC is the ion-exchange capacity in the units of milliequivalent/g (mEq/g).

#### Permeability Measurements of the Polymer Blends

The permeability of pure methanol across the different types of acid-base and covalently

Sample	Membrane Type	Composition (% w/w)	Thickness (µm)	IEC (mEq/g)	$\begin{matrix} {R_{\rm sp}^{\rm H}}^+ \\ (\Omega{*}cm) \end{matrix}$	SW (%)
PSU/PSU <sup>(c.c.)</sup>	c.c.	80 PSU(SO <sub>3</sub> Li) <sub>0.8</sub> 20 PSU(SO <sub>2</sub> Li) <sub>1</sub>	100	1.19	27.2	29.7
PEEK/PSU	i.c.	37.5 $\mu$ I I-(CH <sub>2</sub> ) <sub>4</sub> -I 75 PEEK(SO <sub>3</sub> H) <sub>0.63</sub> 25 PSU(NH)	40	1.32	47.4	20.8
PSU/PSU	i.c.	$20 \text{ PSU}(\text{NH}_2)_{1.7}$ 80 PSU(SO <sub>3</sub> Li) <sub>0.8</sub> 20 PSU(NH <sub>2</sub> ) <sub>4</sub> -	70	1.27	65.34	16.8
PEEK/PBI	i.c.	85 PEEK(SO <sub>3</sub> Li) <sub>0.87</sub> 15 PBI	40	0.9	16.4	28.6
PSU/PBI	i.c.	85 PSU(SO <sub>3</sub> Li) <sub>1.5</sub> 15 PBI	30	1.46	16.5	43.3
Nafion 117			180	1	7.7	16.6

Table I Data of the Investigated Membranes

crosslinked blend membranes was investigated at a temperature of 40°C.

Figure 4 shows the measured permeation flux densities of methanol versus time for the PSU/PBI, the PEEK/PBI, the PSU/PSU<sup>(c.c.)</sup>, the PEEK/PSU, and the PSU/PSU membrane. Additionally, Figure 4 shows the permeation measurement of a Nafion 117 membrane.

The permeation graph of the Nafion membrane first goes through an unsteady state por-



**Figure 4** Methanol flux density as a function of time for a Nafion 117 membrane, a covalently crosslinked blend membrane and different acid-base blend membranes. For details, see text.

tion; then, after a time, the membrane becomes saturated, and the permeation rate remains constant (steady-state part of the permeation process). In comparison, some of the acid-base blend membranes show a different time behavior. After the unsteady-state portion the permeation flux rises to a weak maximum, then the permeation rate decreases, and later the membranes become saturated. A possible explanation of this behavior can be the change of the diffusion process by the absorption of methanol molecules in the membrane and their influence on the diffusion coefficient.<sup>12,13</sup> At the beginning of the diffusion at low methanol concentrations the ionogenic groups promote the diffusion of the polar methanol molecules. In the later stage, with increased methanol concentrations, the ionogenic groups-as in the model of Gierke<sup>14,15</sup>—are partially shielded by absorbed polar methanol molecules, and the effective inner surface density of the ionogenic groups is diminished. This local effective surface density that is eventually formed depends on the local methanol concentration. The total nonlinear diffusion process can, therefore, be seperated into the phase of a strong increase of the diffusion function D(c) by widening the polymeric microstructure (swelling) and a following reduction of D(c) by the reduction of the effective inner surface density of the ionogenic groups. Together, both effects lead to the observed behavior of the methanol fluxes versus time, as shown in Figure 4.

To compare the methanol crossover of the different polymer membranes, the steady-state per-

Sample	Normalized Steady-State Flux (g(MeOH)/cm <sup>2</sup> s)	Normalized Steady-State Flux (g(MeOH)cm/cm <sup>2</sup> s)	Retention Coefficient
Nafion 117	$2.4\cdot10^{-5}$	$4.3\cdot10^{-7}$	1.0
PSU/PBI	$3.0\cdot10^{-6}$	$5.4\cdot10^{-8}$	8.0
PSU/PSU <sup>(c.c.)</sup>	$2.5\cdot10^{-6}$	$4.6\cdot10^{-8}$	9.6
PEEK/PBI	$1.6\cdot10^{-6}$	$2.9\cdot10^{-8}$	15.0
PEEK/PSU	$8.5\cdot10^{-7}$	$1.5\cdot10^{-8}$	28.2
PSU/PSU	$7.5\cdot10^{-7}$	$1.3\cdot 10^{-8}$	32.0

 Table II
 Normalized Methanol Permeation Flux and Retention Coefficient of the Investigated

 Membranes

meation rates must be normalized to the same foil thickness.

As a result of the steady-state solution of the 2. Fick law, the steady state flux  $j_s$  is inversely proportional to the foil thickness L:<sup>13</sup>

$$j_s \propto 1/L$$
 (3)

Table II shows the steady-state flux densities normalized to the foil thickness of Nafion (180  $\mu$ m) in the units g(MeOH)/cm<sup>2</sup>s, and for comparison, the steady-state flux densities in the units g(MeO-H)cm/cm<sup>2</sup>s. In column 4 of Table II the retention coefficients as the ratio of the steady-state flux of the Nafion membrane to the different acid-base and covalently crosslinked blend membranes are given. The Nafion 117 membrane shows a steadystate permeation rate of  $2.4 \cdot 10^{-5}$  g(MeOH)/cm<sup>2</sup>s. The different types of acid-base and covalently crosslinked blend membranes show a significant reduction of the methanol crossover. The PSU/ PBI membrane, with a thickness of 30  $\mu$ m, has a steady-state permeation rate of  $3.0 \cdot 10^{-6}$ g(MeOH)/cm<sup>2</sup>s, and the covalently crosslinked PSU/PSU<sup>(c.c.)</sup> membrane shows a constant permeation rate of  $2.5 \cdot 10^{-6}$  g(MeOH)/cm<sup>2</sup>s. The acidbase PEEK/PBI, PEEK/PSU, and PSU/PSU blend membranes show a further strong reduction of the methanol crossover. In the case of the PSU/ PSU membrane,  $j_s$  decreases to  $7.5 \cdot 10^{-7}$ g(MeOH)/cm<sup>2</sup>s. In comparison to a Nafion foil, the steady-state rate of methanol is reduced by a factor of about 30.

All the investigated arylene main-chain polymer membranes show a significant lower MeOH permeability than the perfluorinated Nafion membrane. We assume that, in the case of the acid-base and covalently crosslinked blend membranes, the swelling is restricted by the crosslinks. This leads, in comparison to the uncrosslinked Nafion membrane to a lower swelling and to a lower MeOH crossover.

#### **Plasma Polymerized Barrier Films**

An alternative approach to reduce the methanol permeability through ionomer membranes is a thin barrier layer plasma polymerized on the surface of the membranes. For the permeation measurements the membranes were placed between the two compartments of the permeation cell with the coated side up.

Figure 5 shows the measured permeation flux



**Figure 5** Methanol flux density as a function of time for (a) an uncoated Nafion 117 membrane, (b) a plasma polymer film deposited from a hexan: $H_2$  mixture ratio of 2:40, and (c) a plasma polymer film deposited from a hexan: $H_2$  mixture ratio of 10:40.

densities of methanol versus time for (a) an uncoated Nafion 117 membrane, (b) a Nafion 117 membrane with a plasma polymer film deposited from a hexan:H<sub>2</sub> mixture ratio of 2:40, and (c) a Nafion 117 membrane with a plasma polymer film deposited from a hexan:H<sub>2</sub> mixture ratio of 10:40. All plasma polymer films have a thickness of approximately 0.3  $\mu$ m.

The steady-state permeation rate  $j_s$  decreases from  $2.4 \cdot 10^{-5}$  g(MeOH)/cm<sup>2</sup>s for the uncoated Nafion membrane to  $3.7 \cdot 10^{-6}$  g(MeOH)/cm<sup>2</sup>s for a plasma polymer film obtained from a hexan:H<sub>2</sub> plasma with a mixture ratio of 2:40. An increase of the hexan concentration during the deposition process leads to a further reduction of the methanol permeability. In the case of a plasma polymer barrier film from a hexan:H<sub>2</sub> plasma with a mixture ratio of 10:40,  $j_s$  decreases to  $2.2 \cdot 10^{-6}$ g(MeOH)/cm<sup>2</sup>s. This means that a 0.3-µm-thick film plasma polymerized on a Nafion foil with a thickness of 180 µm reduces the methanol crossover by a factor of about 10.

A plasma polymer film deposited from a pure hexan plasma shows a steady-state permeation rate similiar to that of the uncoated Nafion membrane. After the permeation experiment many cracks in the plasma polymer film were observed. The reason for this mechanical damages are the different expansion coefficients of the plasma polymer layer and the Nafion membrane. The addition of hydrogen during the deposition process as in the case of the mixture ratio of 10:40 leads to a slower growth of the plasma polymer films. A relatively soft and flexible layer results.

Figure 5 shows that the permeation rate of an uncoated Nafion membrane rises to the steady state within about 500 s. In comparison, the coated membranes attains steady state within about 1000 and 2000 s. This means that if the steady-state permeation flux decreases, the time required to attain steady state increases. These differences in the time behavior are due to the concentration dependence of the diffusion coefficient.<sup>8,16</sup>

In a previous work, the chemical composition of such CH— plasma polymer films were investigated by Fourier transform Infrared spectroscopy and XPS measurements.<sup>17</sup> It was demonstrated that the chemical composition of the barrier layers is similar to that of polyethylene.<sup>18</sup> The permeation process of methanol molecules through Nafion involves the solution of the liquid at the upstream face, followed by diffusion through the foil, and desorption from the downstream face.<sup>12,13,19</sup> This means that the permeation rate mainly depends on the diffusion and solution coefficient. In a simplified description the thin plasma polymer film causes a decrease of the sorbed methanol molecules in the polymer matrix related with a decrease in the permeation rate. The plasma polymer layer acts as a solvent barrier layer.<sup>19</sup>

# CONCLUSION

This investigation contributes to the problem of methanol crossover through ionomer membranes. Such membranes are used as polymeric electrolytes in direct methanol fuel cells. The primary results shown here are:

- 1. In comparison to Nafion, the investigated acid-base and covalently crosslinked blend membranes show a significant lower methanol crossover. The steady-state flux decreases from  $2.4 \cdot 10^{-5}$  g(MeOH)/cm<sup>2</sup>s for a Nafion membrane to  $7.5 \cdot 10^{-7}$  g(MeOH)/cm<sup>2</sup>s for a PSU-SO<sub>3</sub>H/PSU-NH<sub>2</sub> membrane.
- 2. Further, it is shown that a thin barrier layer deposited from hexan:H<sub>2</sub> plasmas is an attractive method to reduce the methanol crossover of Nafion. For example, a plasma polymerized film with a thickness of 0.3  $\mu$ m reduces the permeability of methanol by an order of magnitude.

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