

Short communication

# Crossover of formic acid through Nafion<sup>®</sup> membranes

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Received 14 December 2002; accepted 30 December 2002

## Abstract

Formic acid has been proposed as a possible fuel for miniature fuel cells, because formic acid is expected to show low crossover and easy water management. In this paper, the permeation of formic acid through Nafion<sup>®</sup> membranes is investigated at room temperature. It is found that the permeation of formic acid through Nafion<sup>®</sup> 112 and 117 is much lower than that of methanol. For example, at a 1 M concentration, the steady state flux of formic acid through Nafion<sup>®</sup> 117 is only  $2.03 \pm 0.07 \times 10^{-8}$  mol/cm<sup>2</sup> s. By comparison, previous workers have observed a methanol flux of  $3$  to  $6 \times 10^{-6}$  mol/cm<sup>2</sup> s through Nafion<sup>®</sup> 117 under similar conditions. The flux through Nafion<sup>®</sup> 117 increases with increasing formic acid concentration, reaching a maximum of  $1.86 \pm 0.11 \times 10^{-7}$  mol/cm<sup>2</sup> s at a formic acid concentration of 10 M. The flux of formic acid is about a factor of two higher through Nafion<sup>®</sup> 112 than through Nafion<sup>®</sup> 117 but still low. These results show that the permeation of formic acid through Nafion<sup>®</sup> is much slower than the permeation of methanol through the same membrane. Consequently, formic acid is an attractive alternative fuel for small polymer electrolyte membrane (PEM) fuel cells.

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**Keywords:** Formic acid; Permeation; Nafion<sup>®</sup> membrane; Fuel cell; Crossover

## 1. Introduction

In previous work we found that formic acid fuel cells show interesting properties for micro power generation [1,2]. In contrast to direct methanol fuel cells [3,4], formic acid fuel cells run well at high formic acid concentrations and give reasonable power output at room temperature [2]. There was no evidence in our initial studies [1,2] of significant formic acid crossover, but the crossover rate was not measured directly.

The purpose of this paper is to quantify the rate of formic acid permeation through Nafion<sup>®</sup> membranes. We chose to examine the properties of bare membranes so that we could tell if the permeability of formic acid through Nafion<sup>®</sup> is small, independent of the catalyst layer. Our procedure is to use a permeation cell similar to those used previously [5,6,8] to measure the flux of formic acid through the Nafion<sup>®</sup> in the absence of an electric field and then compare to the previous results to see if the permeation of formic acid is small. We chose to use a permeation cell, rather than an electrochemical measurement [3,4,9–15] so that we could avoid

complications due to electric fields, reactions in the catalyst layer or CO<sub>2</sub> crossover [16]. All of the work was done at room temperature since formic acid fuel cells are projected to run at room temperature.

## 2. Experimental

The permeation experiment involved putting a formic acid solution on one side of a membrane, putting distilled water on the other side of a membrane, and measuring the flux through the membrane as a function of time. The permeation measurement fixture was designed and built in house. The fixture has two glass compartments, whose volumes are approximately 40 ml. They are separated by a Nafion<sup>®</sup> membrane supported by two *o*-rings at both sides. Two teflon membrane holding structures containing the *o*-rings have male and female screws and can be easily combined by rotating them tightly. Silicon lubricant and teflon tape were used to combine teflon pieces and glass compartments. Three sets of the fixture were used simultaneously for each experiment to secure the reproducibility. Nafion<sup>®</sup> membranes (112 and 117) were preconditioned prior to use in a permeation measurement fixture as follows: (1) boil in 5% hydrogen peroxide at 80 °C for 1 h; (2) rinse; (3) boil in millipore water for 1 h; (4) boil in 0.5 M H<sub>2</sub>SO<sub>4</sub> at

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80 °C for 1 h; (5) rinse; and (6) boil in millipore water for 1 h. The membrane samples were stored in millipore water prior to use.

Preconditioned Nafion<sup>®</sup> membrane was carefully cut to fit into the teflon structures. The procedure of combining the permeation measurement fixture should be finished as quickly as possible since the membrane tends to get dehydrated easily. After combination, 35 ml of distilled water was filled into one compartment A and 35 ml of formic acid solution into the other compartment B. Careful inspection was done to check for the presence of air bubble inside the teflon structures near the membrane. The permeation rates were artificially low when there were air bubbles near the membrane, since the bubbles inhibit the mass transfer. Also, we observed the solution level in compartment B increased during the experiment. So, compartment B was modified to read the volume change with time, by attaching a burette stem. The pH value and temperature in the compartment A were measured with time using a pH meter (model Accumet AP61, Fisher Scientific). Four formic acid solutions (Aldrich, 96% ACS grade) of 1, 5, 10, and 20 M were tested. A 20 M solution contains 75 wt.% formic acid. The pH meter was standardized frequently with buffer solutions of pH 2, 4, and 7 (Fisher, pH 2 ± 0.02, pH 4 ± 0.01, pH 7 ± 0.01, certified grade).

### 3. Results

Fig. 1 shows some typical data. In this experiment, a 1.131 cm<sup>2</sup> Nafion<sup>®</sup> 117 membrane was loaded into the cell, one side of the cell was filled with various concentrations of formic acid, and the other side was filled with distilled water. Next, the concentration of formic acid in compartment A was measured as a function of time.

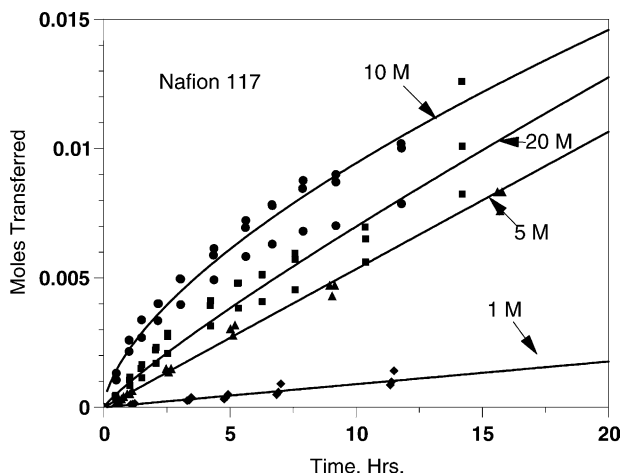


Fig. 1. The amount of formic acid transferred through a 1.131 cm<sup>2</sup> Nafion<sup>®</sup> 117 membrane as a function of time, starting with (◆) 1 M, (▲) 5 M, (●) 10 M and (■) 20 M formic acid. The best fit of the data to a power law model is also shown.

Generally, there is a slow buildup of formic acid in the water solution. The curves for 1 and 5 M fit straight lines through the origin with regression coefficients of 0.961 and 0.984, respectively, showing that the flux of formic acid is approximately constant during the 1 and 5 M experiments. However, the curves for 10 M shows a downward curvature, showing that the permeation is slowly decreasing during the experiment. There are also some sample to sample variations in the permeation rates. One of the Nafion<sup>®</sup> 117 samples showed about 10% less permeation than the other two.

There is more variation in the 20 M curve, but the data seems to show a reproducible decrease in slope with time, suggesting that the permeability of the membrane is decreasing during the course of the experiment. Also, there is an unusual effect that the more formic acid permeates when the formic acid reservoir is filled with 10 M formic acid than with 20 M formic acid. Overall, the permeation rate through the membrane is very slow. With a 20 M (i.e. about 75% by weight) formic acid solution, it takes about 4 days to transfer 0.03 mol/cm<sup>2</sup> of formic acid.

Fig. 2 shows similar data for a Nafion<sup>®</sup> 112 membrane. In this case the flux is larger than with Nafion<sup>®</sup> 117, but still small. With a 10 molar formic acid solution, it takes about a day to transfer 0.03 mol/cm<sup>2</sup> of formic acid. The data in Fig. 2 look somewhat different than those in Fig. 1 in that the curves show much more non-linearity which suggests that the Nafion<sup>®</sup> 112 membrane changes significantly during the course of the experiment.

Table 1 summarizes the data in greater detail. Generally, the permeation rates increase with increasing formic acid concentration, reaching a maximum at 10 M and then decline. Permeation rates are higher with Nafion<sup>®</sup> 112 than with Nafion<sup>®</sup> 117, but drop with time and show complex variations with concentration. In all cases the permeation rates are small.

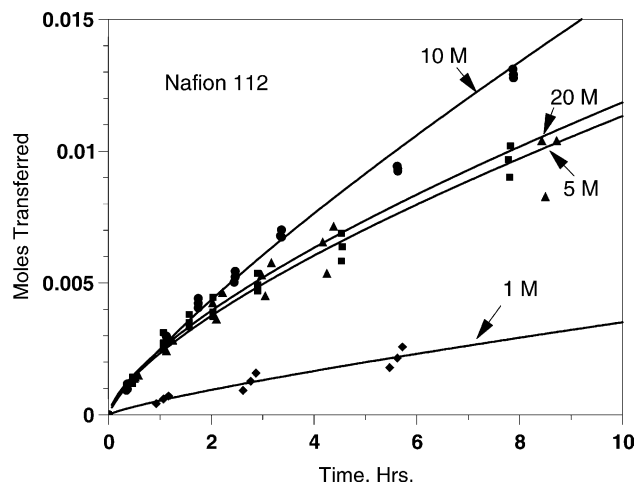


Fig. 2. The amount of formic acid transferred through a 1.131 cm<sup>2</sup> Nafion<sup>®</sup> 112 membrane as a function of time, starting with (◆) 1 M, (▲) 5 M, (●) 10 M and (■) 20 M formic acid. The best fit of the data to a power law model is also shown.

Table 1  
Fluxes of formic acid in Nafion<sup>®</sup> membranes

		Formic acid concentration (M)			
		1	5	10	20
Nafion <sup>®</sup> 117	Flux ( $10^{-8}$ mol/cm <sup>2</sup> s)	$2.03 \pm 0.07$	$12.3 \pm 0.3$	$18.6 \pm 1.1$	$17.0 \pm 1.2$
Nafion <sup>®</sup> 112	Flux from 3 to 20 h ( $10^{-8}$ mol/cm <sup>2</sup> s)	$5.49 \pm 0.37$	$40.6 \pm 4.0$	$45.7 \pm 3.9$	$34.7 \pm 2.6$

The results were calculated from a linear regression of the data.

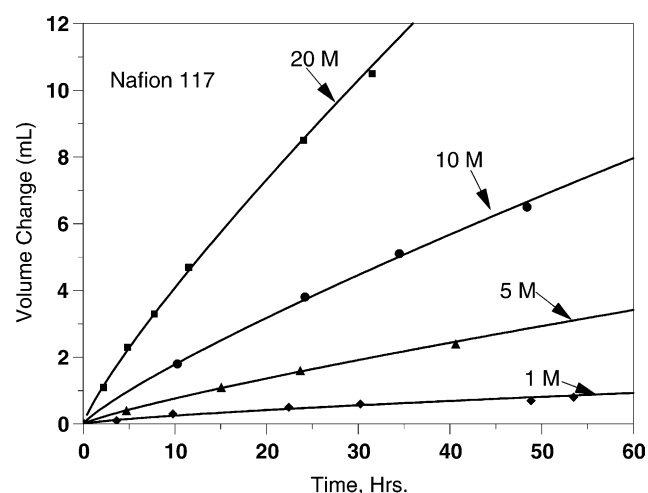


Fig. 3. The volume change in a compartment containing the formic acid solution during the experiments in Fig. 1.

The volume of liquid in the formic acid reservoir was also measured during the experiments in Fig. 1. Fig. 3 shows the effect of formic acid concentration on the volume change in formic acid reservoir. Generally, there is a flux of water from the water reservoir into the formic acid reservoir during the course of these experiments. Physically, formic acid solutions are fairly hygroscopic, so osmotic pressure draws water into the formic acid reservoir over several hours.

Experimentally, the flux of water increases with the increasing formic acid concentration, as expected from the osmotic pressure however, the data in Fig. 3 is not quite as expected. Theoretically, the slopes of each curve in Fig. 3 should remain constant and proportional to the concentration. However, the curves are not linear and their slopes tend to decrease suggesting a slow change in the membrane. When the initial slopes are compared, the slopes of 1, 5, and 10 M are approximately 1, 5 and 10 and are proportional to the concentration. However, the initial slope of 20 M shows a much higher value of approximately 27, indicating that there is extra water being removed from the membrane or water reservoir at short times when 20 M formic acid is used.

#### 4. Discussion

The results here explain, in part, why formic acid fuel cells performed so well in our previous experiments [1,2].

Notice that the formic acid fluxes in Table 1 are all relatively low. At a 1 M formic acid concentration, we observe a flux of only  $2.03 \pm 0.07 \times 10^{-8}$  mol/cm<sup>2</sup> s. By comparison Jung et al. [6] report a methanol flux of  $3.55 \times 10^{-6}$  mol/cm<sup>2</sup> s under similar conditions while Dimitrova et al. [7] report that with a 1.5 M methanol solution about  $7 \times 10^{-6}$  mol/cm<sup>2</sup> s diffuse through a Nafion<sup>®</sup> 117 membrane at 25 °C. Cruickshank and Scott [8] reported that the permeation rate of water, methanol and water–methanol mixture through Nafion<sup>®</sup> 117 were of the order of  $10^{-6}$  mol/cm<sup>2</sup> s. Evidently, the permeation of formic acid through Nafion<sup>®</sup> 117 is much less than that of methanol under similar conditions, which makes crossover less of an issue with a formic acid fuel cell than with a direct methanol fuel cell.

Still, the permeation rates measured here are larger than those inferred from data in a working fuel cell [1,2] presumably because we use up some of the formic acid in the catalyst layer when the cell is operating. A flux of  $2.03 \pm 0.07 \times 10^{-8}$  mol/cm<sup>2</sup> s, corresponds to a crossover current of 3.9 mA/cm<sup>2</sup>, i.e. small but not negligible.

We also observe that water osmotic pressure draws water into the formic acid reservoir over several hours. Flooding of direct methanol fuel cells often limits DMFC room temperature performance. That seems to be less of an issue with formic acid fuel cells due to the osmotic pumping.

It is interesting to speculate why the permeation rate of formic acid through Nafion<sup>®</sup> is so much less than that of methanol. Recall that previous workers [17] have shown that cations diffuse rapidly through Nafion<sup>®</sup>, while anions are inhibited. Formic acid partially dissociates in solution, forming a formate anion [HCOO]<sup>-</sup>. The anion should only diffuse slowly through Nafion<sup>®</sup>. In contrast, methanol can react with protons on platinum to form methoxonium [CH<sub>3</sub>OH<sub>2</sub>]<sup>+</sup> cations [18–20]. The cations should diffuse rapidly through the Nafion<sup>®</sup> layer. A second effect is that methanol will wet Teflon (i.e. the backbone in Nafion<sup>®</sup>) while formic acid does not. Evidently, the combination of these two effects limits the permeation of formic acid through the Nafion<sup>®</sup> layer.

Those cannot be the entire effect, however. Notice that Fig. 2 shows that the flux of formic acid through Nafion<sup>®</sup> 112 decreases with time. The decrease is larger than one would expect from dilution of the formic acid due to back-diffusion of water. Such a result is not expected if the membrane properties are constant. Table 1 shows that the flux varies non-linearly with concentration. If the membrane

properties were constant, one would expect the permeation rate to be proportional to the concentration of formic acid. Also, theoretically, one would expect the flux of formic acid to be inversely proportional to the membrane thickness [21]. The data in Table 1 show that the flux of formic acid through Nafion<sup>®</sup> 112 is only 1.8–2.3 times that through Nafion<sup>®</sup> 117. Yet the thickness ratio is 3.5. All of these results suggest that the membranes are changing during the course of the experiments, and that the changes limit the diffusion of formic acid through the membranes.

It is not unreasonable that concentrated formic acid solutions could change Nafion<sup>®</sup>. Recall that we have previously shown [22] that methanol pretreatments could change the transport properties of Nafion<sup>®</sup>. Formic acid is very hydrophilic. Therefore, it is not unreasonable that formic acid would change the transport properties of Nafion<sup>®</sup> too.

We suspect that concentrated formic acid solutions dehydrate a thin layer near the surface of a Nafion<sup>®</sup> membrane, and the thin dehydrated layer inhibits further transfer of formic acid. Formic acid is very hydrophilic. Fig. 3 shows that a 20 M formic acid solution draws water out of the water reservoir. Clearly, there is a significant driving force for removal of water from the membrane. Experimentally, Rice et al. [1] found that when a formic acid fuel cell was run in 20 M formic acid, the cell resistance increases with time. Such a result is consistent with the idea that the dehydration of the membrane occurs in concentrated formic acid solutions, and the dehydrated membranes are less able to transport ions. We do not know what happens with 10 M solutions since the membrane resistance does not rise substantially with time. Still, the flux of formic acid decreases, suggesting that the membrane is changing in a way that limits formic acid cross over.

The low permeation rate of formic acid through Nafion<sup>®</sup> membranes observed here supports advantages in using the formic acid for PEM fuel cell. Due to its low crossover, the overall cell performance will not be degraded by cathode poisoning. Hence, in formic acid fuel cell, we do not have to make much efforts to modify the membrane to lessen the crossover like in the direct methanol fuel cell. Also, the low permeation of formic acid through Nafion<sup>®</sup> membranes gives a higher operational concentration range.

## 5. Conclusion

The permeation rate of formic acid through Nafion<sup>®</sup> membranes was directly measured in a house-built permeation measurement device. We find that the permeation rate of formic acid through Nafion<sup>®</sup> membranes ranged from  $2.0 \times 10^{-8}$  to  $4.6 \times 10^{-7}$  mol/cm<sup>2</sup> s depending on the formic acid concentration and membrane thickness. These rates

are much lower than that of methanol reported in the literature [6–8]. Further confirmatory work is under consideration. The low permeation rate of formic acid supports the promising future of formic acid fuel cell development.

## Acknowledgements

This material is based upon work supported by the Defense Advanced Research Projects Agency under US Air Force grant F33615-01-C-2172. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the US Air Force, or the Defense Advanced Research Projects Agency.

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