# Dissolution of Nafion® membrane and recast Nafion® film in mixtures of methanol and water

Z. Siroma*, N. Fujiwara, T. Ioroi, S. Yamazaki, K. Yasuda, Y. Miyazaki

*Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan*

## Abstract

In order to estimate the durability of Nafion® membrane as an electrolyte for direct methanol fuel cells (DMFCs), the degree of dissolution of Nafion® membranes in mixtures of methanol and water at various temperatures up to 80 °C was examined. At 80 °C, more than 30% of the membrane was dissolved in mixed solvents with methanol concentrations of higher than 80%. Dissolution of recast films made from Nafion® solution was also examined, because it is an important component of the catalyst layers of DMFCs. The effects of heat treatment on the durability of the recast films were also examined. Although high temperature (160 °C for 1 min) or long time (120 °C for 1 h) heat treatment improved significantly the durability at room temperature, the films were dissolved at 80 °C and the amounts of dissolution were larger than that of Nafion® 117 membranes.
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## 1. Introduction

Direct methanol fuel cells (DMFCs) using a proton exchange membrane as electrolyte is a potential option for electricity generation, due to their high energy density and simplicity of operation compared with systems using a reformer to produce hydrogen from liquid fuel. DMFC technology is based on a proton exchange membrane fuel cell (PEMFC), in which a polymer electrolyte membrane is used as the electrolyte. However, the state-of-the-art electrolyte membranes are far from the practical stage for DMFCs. For PEMFCs, perfluorosulfonate ionomer (PFSI) membranes such as Nafion® are usually adopted as the electrolytes. However, PFSI membranes exhibit considerable methanol uptake [1–6] and permeation [7,8], and hence the use of them for DMFCs causes a fuel crossover problem [9–13], which leads to deterioration of efficiency and damage to the membrane-electrode assembly (MEA) owing to volume expansion of the membrane. Furthermore, because the catalytic activity for methanol oxidation is low, high temperature (>100 °C) operation may be required for DMFCs [14], but it is difficult to use PFSI membranes above 100 °C, due to the difficulty with water management and lack of long time durability. Considering these viewpoints, many

research works for developing new electrolyte membranes have been done [15–17].

In spite of these restrictions, the PFSI membranes are still widely used for experimental tests in developing DMFCs. In this study, we discuss another factor that may limit the usage of PFSI for DMFCs. It is known that PFSI membranes are soluble in solvents depending on the kind of the solvent and temperature [1,2,18]; especially, recast films of PFSI made from alcoholic solutions are quite soluble [19,20]. For PEMFCs or DMFCs, the PFSI electrolyte is used not only as a membrane between the anode and cathode, but also as an important component of the gas diffusion electrodes to improve their reactivity, which is usually realized by using commercially available PFSI solution as a raw material to form the catalytic layer. Therefore, in DMFC studies, the durability of the electrolyte in methanol solution has to be considered during operation of the cell. This is true not only for the PFSI membrane but also for the recast PFSI inside electrodes, and even in fundamental experiments such as rotating disk electrodes using recast PFSI film. Here, we report the degree of the dissolution of the bulk membranes and recast films of Nafion® in mixtures of methanol and water in various ratios and at various temperatures up to 80 °C. Durability of the recast films in solvents is known to be improved by heat treatment [21–23], and hence the effect of heat treatment temperature on the dissolution of the films was also examined.

* Corresponding author. Tel.: +81-72-751-9653; fax: +81-72-751-9629.
*E-mail address:* siroma.z@aist.go.jp (Z. Siroma).

## 2. Experimental

For the dissolution tests of the bulk membranes, acid type Nafion® 117 membranes (175 μm thick, du Pont de Nemours) were used. Prior to use in dissolution tests, the membrane was treated serially in hydrogen peroxide solution (3 wt.%), water, sulfuric acid (1 mol dm$^{-3}$), and finally water, each for 1 h at 80 °C. The membrane was then cut into pieces of 1 cm × 2 cm. The samples were dried overnight under vacuum at room temperature, followed by measurements of the weights. To avoid changes in weight during measurements, the samples were weighed in a dry glove box immediately after vacuum drying. Mixtures of methanol (99.8 %, Wako Pure Chemical Industries) and water in various ratios including pure water and pure methanol were prepared for the dissolution tests. Each sample was put into a glass vial with 40 cm$^3$ of a mixed solvent. During the dissolution tests, the vials were kept for 1 week at room temperature (25 °C) or at elevated temperatures (35–80 °C) in thermostatic oven (ESPEC, PHH-101). After the dissolution tests, the dimensions of each sample were measured again to calculate volume expansion. Samples were then dried under vacuum at room temperature overnight again, followed by measurements of the weights. The term "dissolved fraction" was determined to be:

$$\text{dissolved fraction} = \frac{m_1 - m_2}{m_1} \qquad (1)$$

where $m_1$ and $m_2$ are the dry weights before and after the dissolution test, respectively. Recast films made from a solution of 5 wt.% Nafion® in a mixture of alcohols and water (equivalent weight (EW) = 1100, Aldrich Chemical) were also used for the dissolution tests. Substrates for casting must be durable in strong acid and have good adhesiveness with the recast films. For these reasons, polytetrafluoroethylene (PTFE) membrane filters (90 mm diameter, 70 μm thickness, pore size: 0.1 μm, Toyo Roshi Kaisha) were used as the substrates. Each sample was made by casting of 2 cm$^3$ of the Nafion® solution on a PTFE membrane filter, followed by drying in ambient environment. Before casting, weight of each membrane filter was measured to determine the precise weight of the recast film. The procedure for the dissolution test for the cast films was the same as that for the Nafion® 117 samples described above. To investigate the influence of the heat treatment on the dissolution durability, some recast samples were hot-pressed between PTFE sheets at given temperatures and periods of time before dissolution tests.

## 3. Results and discussion

The dissolved fractions and volume expansions of the Nafion® 117 samples at various temperatures after 1 week are plotted as functions of methanol concentration in Figs. 1 and 2, respectively. At each temperature in this range, the dissolved fractions show a maximum at a concentration of
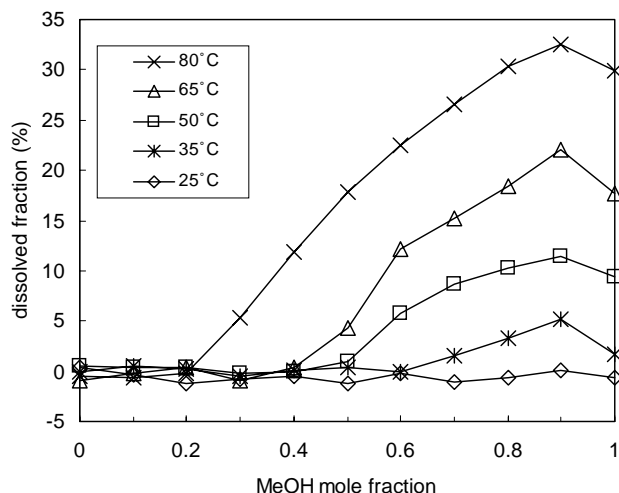


Fig. 1. Dissolved fractions of the Nafion® 117 samples after dissolution tests in mixed solvents of water and methanol at various temperatures and concentrations for 1 week plotted as a function of the concentration of methanol.

methanol:water = 9:1. There seems to be a correlation between the dissolved fraction and volume expansion. The dissolved fractions are plotted against the volume expansions in Fig. 3. Gebel et al. [1] and Gebel and Aldebert [2] reported that the dissolved amount was mainly related to the degree of swelling, but did not depend on the kind of solvent or the temperature. They showed a critical value of $V_s/V_p \sim 2$, above which Nafion® was dissolved, where $V_s$ and $V_p$ are the solvent and polymer volumes, respectively. In Fig. 3, the point when the volume expansion = 3 corresponds to $V_s/V_p = 2$. Though our results did not show a clear relation between the volume expansion and the dissolved fraction, dissolution was observed only when the volume expansion > 3. The expansion of the samples showed anisotropy. Linear expansions after the dissolution test at 80 °C are shown in Fig. 4. In the figure, "length" and
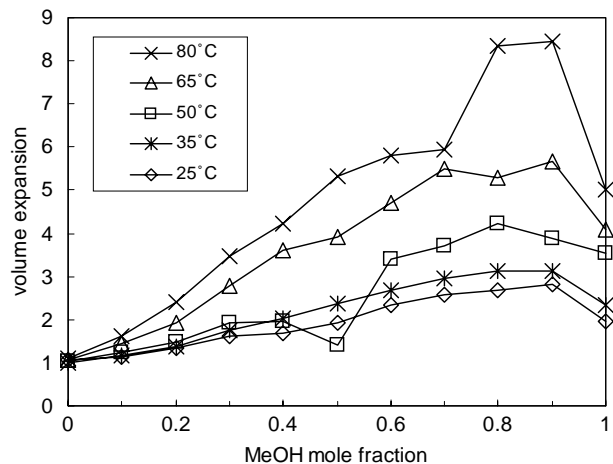


Fig. 2. Volume expansions of the Nafion® 117 samples after the dissolution tests shown in Fig. 1.
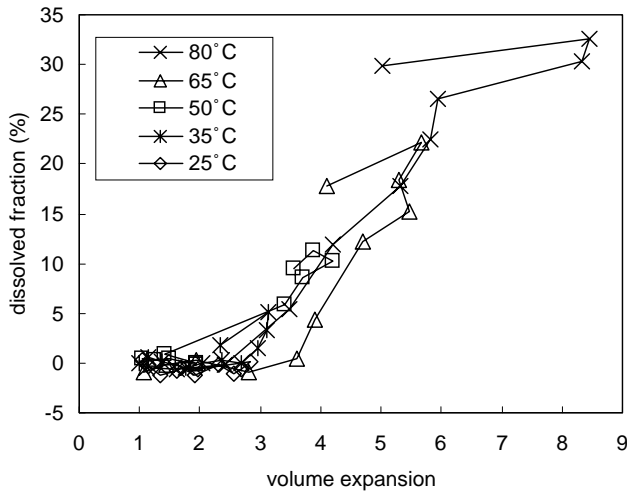
Fig. 3. Relations between the dissolved fraction and volume expansion.

"width" mean the dimensions in directions parallel and perpendicular to the laminating direction of the Nafion®, respectively. The expansion in thickness was smaller than that in the other directions. Furthermore, expansion in width was slightly larger than that in length. This slight difference is not an experimental error, because every sample showed the same tendency. However, it might be due to the shape of the sample, because every sample was cut to a length of 2 cm and a width of 1 cm, not a square. From Fig. 1, it is observed that at 80 °C, which is a common operating temperature of PEMFCs, the membrane is dissolved by solvents containing methanol higher than 20 mol%. Even at 35 °C, which is a possible temperature of portable devices, a solvent containing methanol higher than 60 mol% dissolves the membrane. Judging from these results, in the operation of a DMFC, one has to consider degradation of the membrane by the
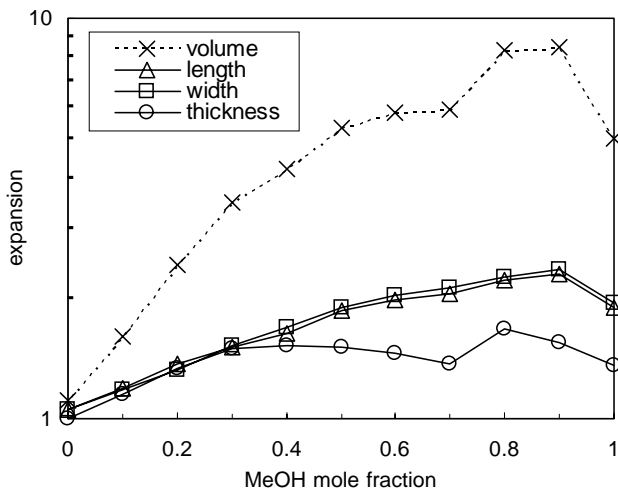


Fig. 4. Logarithms of the linear expansions along the three directions and volume expansions (sum of the three linear expansions in this log plot) of the samples after dissolution test at 80 °C. See text for the directions expressed as 'length' and 'width'.
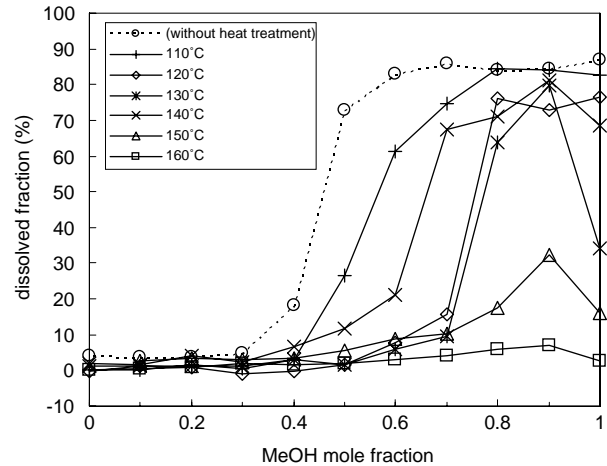


Fig. 5. Dissolved fractions of heat-treated recast Nafion® films after a dissolution test at room temperature for 1 week. Each line shows the results after heat treatment at the same temperature. Results for the samples without heat treatment are also shown (dotted line).

fuel solution, depending on the temperature and methanol concentration. The concentrations mentioned above are by far higher than those of the fuel solution usually adopted for the DMFCs. However, the use of concentrated fuel as high as possible is preferable to increase the energy density, especially for portable DMFC systems to minimize the balance-of-plant. The stoichiometric methanol concentration for the anode reaction of DMFCs is 50 mol%; therefore, the scope of using highly concentrated fuel may come to this level.

The dissolved fractions of the recast Nafion® samples after 1 week at room temperature are plotted in Fig. 5. Before the dissolution tests, the samples were heat-treated at several temperatures in the range of 110–160 °C for 1 min. Samples without heat treatment were also examined, and almost every portion of them was dissolved by solvents of methanol concentrations higher than 50 mol%. Samples treated at 160 °C were not appreciably dissolved by any of the solvents. In contrast, any samples heat-treated at temperatures lower than 160 °C were somewhat dissolved by highly concentrated solvents. On the other hand, even a heat treatment at 110 °C improved dissolution resistance in some degree by comparison with the samples without heat treatment. Figs. 6 and 7 show the effects of the time for heat treatment at 120 and 110 °C, respectively. At 120 °C, the improvement in dissolution resistance was still in progress at 10 min, followed by the attainment of sufficient resistance at 1 h. On the other hand, samples treated at 110 °C for even 1 h were very soluble.

The results in Figs. 5 and 6 show that recast films after a sufficient heat treatment are not dissolved at room temperature. As was shown in Fig. 1, a Nafion® 117 membrane was not dissolved at room temperature, but it was soluble at 80 °C in some solvents. Therefore, it is natural to expect that even a sufficiently heat-treated recast film is still soluble at
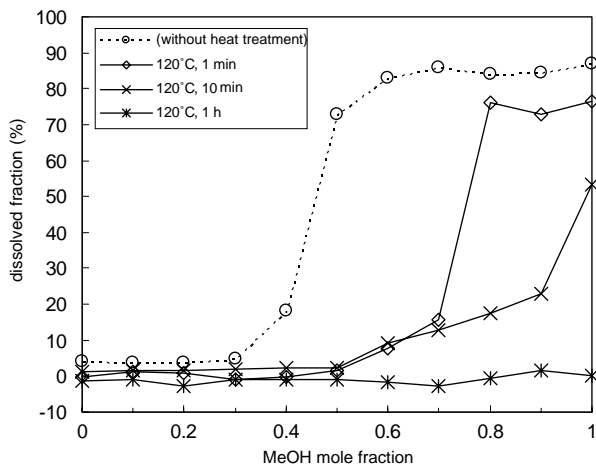
Fig. 6. Dissolved fractions of 120 °C-treated recast Nafion® films at room temperature for 1 week. The time for the heat treatment was varied.
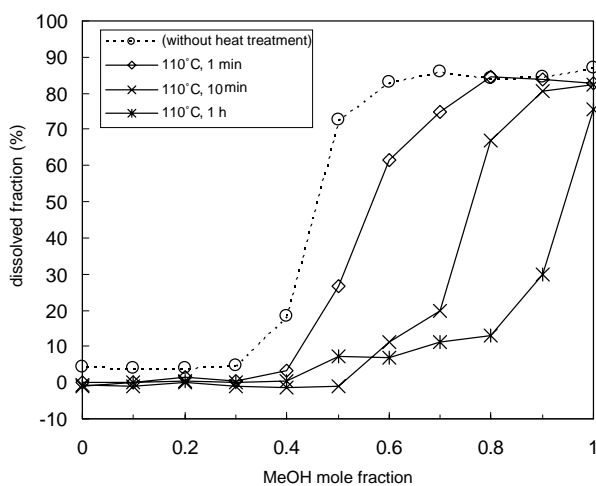


Fig. 7. Dissolved fractions of 110 °C-treated recast Nafion® films at room temperature for 1 week. The time for the heat treatment was varied.
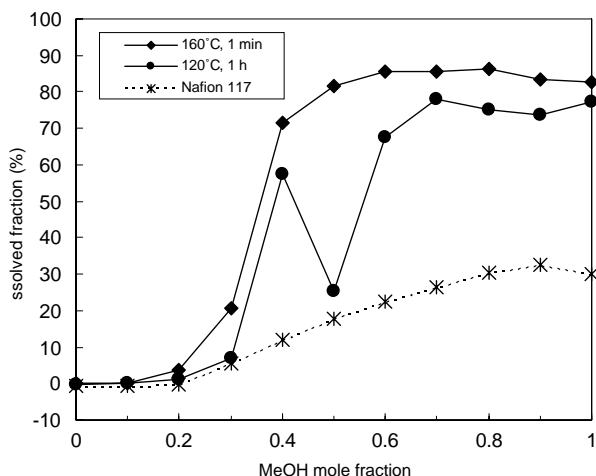


Fig. 8. Dissolved fractions of heat-treated recast Nafion® films after a dissolution test at 80 °C. Heat treatments were at 160 °C for 1 min or at 120 °C for 1 h. The results of Nafion® 117 samples under the same conditions are also shown.

80 °C. Dissolved fractions at 80 °C of recast films treated at 160 °C for 1 min or at 120 °C for 1 h are shown in Fig. 8. The results for Nafion® 117 shown in Fig. 1 are also plotted for comparison. It is clear that sufficiently heat-treated recast films are soluble at 80 °C, and the amounts of dissolution were more significant than those of the Nafion® 117 samples. Heat treatment is believed to change the inner structure of the recast film toward that like the bulk Nafion® membrane, which results in an increase in crystallinity, mechanical strength and the resistance to the dissolution and permeation [21–23]. However, it was shown by our experiments that the resistance to dissolution of recast films with heat treatments do not reach the extent of that of the bulk membrane.

## 4. Conclusions

Degrees of dissolution of bulk membranes and recast films of Nafion® in methanol/water mixtures were examined. At 80 °C, solvents containing methanol higher than 20 mol% dissolved the Nafion® membrane, and 90 mol% methanol gave the maximum value of the dissolved fraction. Even at 35 °C, solvents containing methanol higher than 60 mol% dissolved the membrane. The dissolution of the membrane was observed when the volume expansion was greater than 3. A large fraction of the recast films was dissolved by a methanol-rich solvent even at room temperature. Heat treatment of the recast film improved the resistance to dissolution. Dissolution tests after heat treatments for constant period (1 min) showed that recast films treated at 160 °C were not dissolved by any of the solvents at room temperature. Another set of dissolution tests after heat treatments at constant temperatures (110 and 120 °C) showed that structural change during the treatment was still in progress at 10 min and that recast films treated at 120 °C for 1 h were not dissolved by any of the solvents at room temperature. Although the recast films treated at 160 °C for 1 min or at 120 °C for 1 h were insoluble at room temperature, they were dissolved at 80 °C and the dissolved fractions were higher than those of Nafion® membrane.

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