

# Conductivity and surface morphology of Nafion membrane in water and alcohol environments

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Received 4 August 2004; received in revised form 1 October 2004; accepted 31 January 2005

Available online 16 March 2005

## Abstract

Effects of methanol, ethanol, 2-propanol and water on the proton conductivity and surface properties of Nafion membrane have been studied by electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM). It was established that both conductivity and surface topography decrease in alcohol environment while they show high values and big roughness when Nafion is in aqueous environment. We have measured the conductivity of Nafion in water–alcohol mixtures environments and results give evidence of conductivity and dielectric constant dependence, which has been explained on the basis of Born and Arrhenius equations. Nafion's surface properties were investigated by contact and tapping AFM modes. Surface topography considerably changes when samples absorb water. However, samples stored in alcohols are characterized by flat surfaces. Surface modification was linked to an expansion phenomenon during the swelling of Nafion by solvents. Tapping mode phase images showed that ionic and cluster domains are distinguishable from the surface of samples impregnated either in water or alcohols.

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*Keywords:* Nafion membrane; Proton conductivity; Activation energy; Surface morphology; Alcohols

## 1. Introduction

Nafion membrane, copolymer of tetrafluoroethylene and perfluorinated vinyl ether containing terminal sulfonyl fluoride group, find applications in various industrial domains due to its important properties. It is used as electrolyte in proton exchange membrane fuel cells (PEMFCs) because it combines high ionic conductivity, high thermal, chemical and mechanical stabilities. In direct alcohol fuel cells (DAFCs) based on PEMFCs, alcohol is not reformed into hydrogen gas but is used directly in a simple type of fuel cell [1] which appear to be the most promising as a battery replacement for portable applications such as cellular phones and laptop computers. The anodic compartment in DAFC is fed by a mixture of alcohol dissolved in water. The alcohol part of the mix-

ture is intended to be oxidized at the anode and water part to participate in anode reaction but also to hydrate Nafion. However, alcohols crossover the membrane from the anode to the cathode resulting in change of the Nafion's swelling conditions but a very few measurements of ionic conductivity were made in these environments.

Proton conductivity of Nafion has been investigated by many groups in different aqueous environments and conditions. Slade et al. summarized the literature data in the recent paper [2]. To the best of our knowledge, only a very few studies [3,4] investigated the conductivity of Nafion in nonaqueous solvents. Doyle et al. [3] measured the ionic conductivity of Nafion in different organic solvents and solvent mixtures. They reported that the most important factors determining the ionic conductivity in membranes swollen by polar nonaqueous solvents are the solvent viscosity, molar volume, donor properties and the solvent uptake by the membrane.

Nafion has been the focus of a large number of experimental studies using different techniques, particularly X-ray,

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NMR, IR and electron microscopy in order to explain the microstructure of the membrane [5]. Many models were given and still suggestions for new ones continue to be proposed and the real structure of Nafion membranes still remains to be clarified.

Using scanning probe microscopy and especially atomic force microscopy (AFM), Nafion membrane in different forms was also investigated by different groups in different conditions. Nafion 117 membranes in sulfonyl fluoride precursor form,  $-(CF_2CF_2)_n-(CF_2CF(OCF_2CF(CF_3)OCF_2CF_2SO_2F))$ , which were rinsed extensively with deionized water and boiled in deionized water for 1 h and dried in a vacuum oven at 130 °C and observed by AFM did not show any contrast characteristics of ionic domains [6]. This was attributed to the nonionic form of the membrane because the polar group phase separation into distinct domains does not occur. It means that the precursor is completely hydrophobic and needs hydrolysis to convert sulfonyl fluoride ( $SO_2$ ) groups to sulfonic ( $SO_3^-$ ) groups. Liquid tapping mode topographic AFM images of Nafion precursor in contact with a hydrolysis mixture showed that there is a change in the surface morphology of the sample only during the first 12 min [7].

Cation forms of Nafion were obtained using different hydrolysis procedures. Then dry or wet samples were imaged at ambient temperature and under ambient or relative humidity [6,8–12]. It was found that a Nafion swelled by water and especially by tributylphosphate exhibited morphological changes. The results particularly showed that tapping mode phase imaging could identify the hydrophobic and hydrophilic regions of the Nafion in its acid or salt form. It was also established that the increase in relative humidity or soaking in water led to an increase in phase contrast of hydrophilic regions. Nafion films prepared by spin-coating technique from Nafion solution showed an irregularly shaped microstructure when they were observed by AFM [13]. However, the microstructure shifted towards an apparently homogeneous structure after 30 min of exposure to methanol vapor. Previously Fan and Bard [14] imaged Nafion thin film spin-coated using scanning electrochemical microscopy (SECM) and reported that SECM can distinguish between zones of different ionic conductivity in a sample. Recently Kanamura et al. [15] combined AFM and surface potential measurement (SPoM) and reported that bright spots in potential images can be assigned to ion channels in the Nafion membrane.

Because there is a continued interest in DAFCs, we are motivated to study the electrical and surface properties of the Nafion membrane in water and alcohol environments. Recently, we have reported the morphology change of Nafion in water and methanol [16]. In the present work, we investigated the effects of methanol, ethanol, 2-propanol, and water on the proton conductivity and surface morphology of Nafion membrane by electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM).

## 2. Experimental

Nafion<sup>®</sup> 117 perfluorinated membrane films, manufactured by E.I. du Pont de Nemours & Co., Inc., were obtained from Aldrich Chemical Company, Inc. The membrane has an equivalent weight 1100 g/ml and thickness of 178  $\mu\text{m}$ . High purity alcohol solvents of methanol, ethanol and 2-propanol were purchased from Nacalai Tesque, Kyoto, Japan. We also used Mill-Q water as pure solvent or mixed with alcohols. The Nafion membranes were pretreated by boiling in 0.5 M  $H_2SO_4$  for 1 h, then boiled in deionized water for 1 h and rinsed thoroughly by deionized water. After that samples are stored in the different solvents cited above.

Conductivity measurements were performed on the acid form of the membrane after storing samples in different solvents for more than 2 days. The impedance cell consisted of the sample fixed between two gold electrodes supported by silicon rubbers and glass plates. To ensure good electrical contact, we used a micrometer under a pressure of about 2 atm. Prior to measurement, membrane films were surface dried with a tissue paper, then quickly inserted between the two gold electrodes and pressed by the micrometer. At least three samples for each solvent were used to determine the reproducibility of the measurements. All measurements were carried out at room temperature under ambient humidity. Ac impedance spectrum was recorded from 10 Hz to 5 MHz using a Solartron 1260 Impedance/Gain-Phase Analyzer and Zplot software for windows. The membrane resistance  $R$  was determined by extrapolating the complex impedance diagram at high frequency to the real axis. The conductivity  $\sigma$  was calculated from the formula  $\sigma = l/RS$ , where  $l$ ,  $R$  and  $S$  denote the sample thickness, the membrane resistance and the sample area respectively.

The films were examined by means of AFM using SPM-9500 J3 model from Shimadzu. It is equipped with a 55  $\mu\text{m}$  scanning head and is operated in the contact and tapping modes. For the contact mode, we used silicon nitride probes (Olympus), with spring constant of 0.57  $\text{N m}^{-1}$  and resonance frequency of 73 kHz. For tapping mode, we used silicon probes (Olympus), with spring constant of 42  $\text{N m}^{-1}$  and resonance frequency of 300 kHz. The AFM observation was conducted at room temperature and room humidity. Under these conditions, the Nafion did not show any surface modification within 24 h after the sample was mounted on a metallic substrate. Based on the experience, the Nafion morphologies were imaged immediately with a scan rate of 1 Hz and 512  $\times$  512 pixel resolution. Calibration of the piezo scanner of AFM was carried out by imaging Gold grating sample from Shimadzu Company.

## 3. Results and discussion

### 3.1. Conductivity study

The results of proton conductivity of samples stored in water, alcohols and mixtures are listed in Table 1. Results show

Table 1

Conductivity of Nafion membrane stored in different solvents and calculated conductivity decrease versus water for each solution versus conductivity in water

Solvent	Conductivity ( $\text{S cm}^{-1}$ )	Relative conductivity decrease (%)
Water	0.1013	
Methanol (MeOH)	0.0206	80
MeOH–H <sub>2</sub> O, 75–25% (vol.)	0.0311	69
MeOH–H <sub>2</sub> O, 50–50% (vol.)	0.0667	34
MeOH–H <sub>2</sub> O, 25–75% (vol.)	0.0912	10
Ethanol (EtOH)	0.0102	90
EtOH–H <sub>2</sub> O, 75–25% (vol.)	0.0195	81
EtOH–H <sub>2</sub> O, 50–50% (vol.)	0.0444	56
EtOH–H <sub>2</sub> O, 25–75% (vol.)	0.0770	24
2-Propanol (2PrOH)	0.0026	97
2PrOH–H <sub>2</sub> O, 75–25% (vol.)	0.0117	88
2PrOH–H <sub>2</sub> O, 50–50% (vol.)	0.0239	76
2PrOH–H <sub>2</sub> O, 25–75% (vol.)	0.0531	48

that conductivity decreases drastically in pure alcohols, and especially with 2-propanol whose conductivity is 40 times lower than that with water. However, results show that for Nafion acid form and even in pure alcohols, the conductivity is still higher than  $1 \times 10^{-3} \text{ S cm}^{-1}$ . In the water–alcohol mixtures, the conductivity increased with increasing the wa-

ter proportion irrespective of the nature of the alcohol. Edmondson et al. [4] placed Nafion samples in contact with water and methanol and reported that the conductivity is generally lower in the water–methanol mixed solution-treated samples than in samples treated with the corresponding amount of water. Table 1 lists conductivity values showing that mixtures with low alcohol content, which correspond to alcohol crossover's conditions through the membrane, have conductivities very close to that in pure water. This signifies that alcohol crossover does not affect the conductivity of the membrane.

The relative conductivity decrease versus water is 78, 89 and 98% in methanol, ethanol and 2-propanol respectively. Doyle et al. [3] found that conductivity of Nafion 117 in its lithium form decreased from 0.0161 to 0.00495  $\text{S cm}^{-1}$  from samples equilibrated with water and methanol, respectively. This corresponds to a relative conductivity decrease of 69%. In our experiments, the decrease in methanol versus water is more important probably because the methanol uptake in acid form is higher than that in lithium form as reported by Yeo and Cheng [18].

To correlate between proton conductivity and dielectric constant, we examined the conductivity data in more detail. The dielectric constants of pure solvents used in this

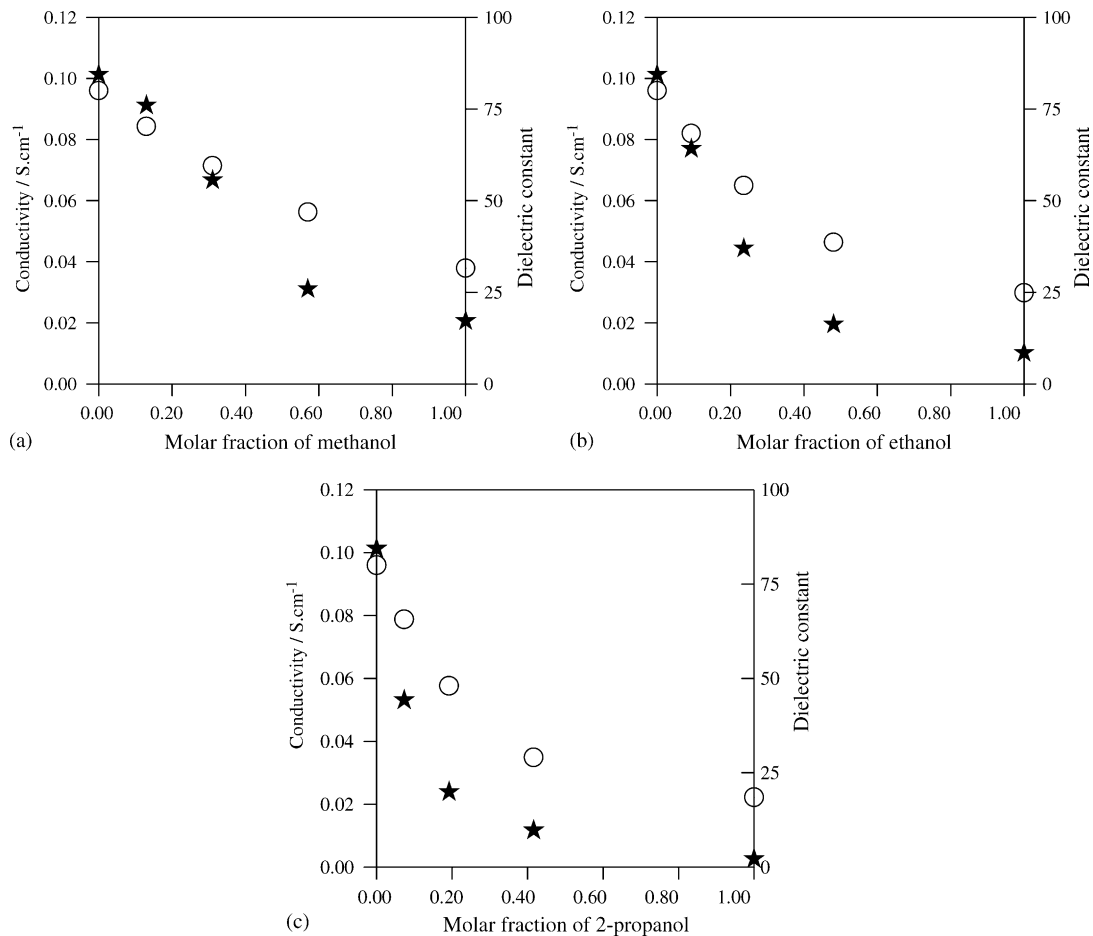


Fig. 1. Proton conductivity (\*) and dielectric constant (O) of Nafion vs. molar fraction of alcohols in water–alcohols mixtures.

study are well known. However, few data have been published on the dielectric constant of water-alcohol mixtures. Akerlof [19] measured the dielectric constant for some mixtures, and Suresh and Naik [20] proposed a model for their calculation. Using these two works [19,20], we could estimate the dielectric constant corresponding to mixtures used in this study. Fig. 1 (a)–(c) shows the proton conductivity and dielectric constant of Nafion versus molar fraction of the different alcohols in water–alcohols mixtures. It is clear that a fair correlation exists between the conductivity and dielectric constant for each mixture separately.

In order to identify trends and relationships between proton conductivity and dielectric constant, we performed curve fitting of conductivity and dielectric constant data of all pure and mixture solvents. The best fitting of data for linear regression has been found with a  $R^2$  of 0.90. When conductivity data are plotted versus  $(1/\varepsilon)$  as shown in Fig. 2, the  $R^2$  of 0.94 is obtained with an exponential decay represented by the following equation:

$$\sigma = 0.221 \exp(-82.375/\varepsilon) \quad (1)$$

We should mention first that Doyle et al. [3] reported in their study related to the Nafion 117 lithium form that conductivity correlates reasonably well with dielectric constant although substantial scatter was apparent. The observed dispersion in their data may be attributed to diversity of used organic solvents. In our study we used only one type of organic solvents namely lower polar alcohols, which may explain, in part, the dependence in our results between conductivity and dielectric constant.

Recently Singh et al. [21,22] proposed an equivalent dependence between the number of free mobile charge carriers  $n$  and dielectric constant  $\varepsilon$ :

$$n = n_0 \exp(-U/2\varepsilon kT) \quad (2)$$

where  $n_0$  represents the pre-exponential factor while  $U$  represents the dissociation energy.

Actually, mobility may be independent to the solvent. However, the solvents used are restricted to alcoholic so-

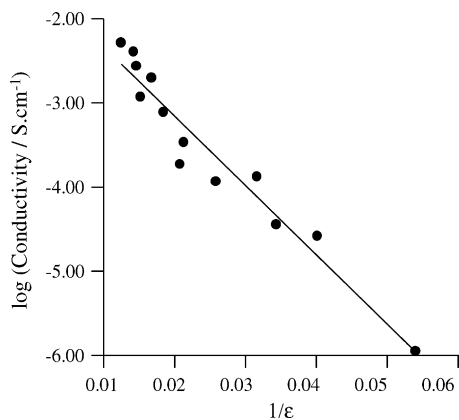


Fig. 2. Proton conductivity as function of the reverse of dielectric constant. Conductivity and dielectric constant data are taken from Fig. 1.

lutions; therefore, we can postulate according to the Eq. (2) that an increase of the number of charge carrier  $n$  lead to an enhancement to the conductivity and consequently conductivity and dielectric constant are linked by a similar equation of that we obtained.

We think that the dependence in Eq. (1) can be explained on the basis of the Arrhenius and Born equations. The relationship between conductivity and temperature can be expressed by the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (3)$$

The Born theory [23] takes into account of solvent polarity effects in the solvation equilibrium and predicts that solvation energy  $\Delta G_{\text{sol}}$  is function of the dielectric constant  $\varepsilon$  of the medium:

$$\Delta G_{\text{sol}} = -(ze_0)^2/2r(1 - 1/\varepsilon) \quad (4)$$

where  $z$  is the charge of ions,  $r$  their radii and  $e_0$  the elementary charge.

If we assume that activation energy for proton transfer results predominantly from solvation energy, like for the case of electron transfer according to Marcus theory [24]. If we also presume that radius variation of solvated ions, which contribute to the proton transfer ( $\text{H}_5\text{O}_2^+$ ), is less important than dielectric constant variation and consequently solvation energy may considered as proportional to the reverse of dielectric constant. Hence, it is reasonable that the conductivity exponentially vary with the reverse of the dielectric constant at a constant temperature.

Our measurements were carried out at room temperature; the fitted equation gave a value of  $0.08 \text{ S cm}^{-1}$  in the case of pure water (Fig. 2). This value has been already measured by different authors and is commonly used as a reference for Nafion conductivity at room temperature. Although we cannot speculate, at this stage, about the function between conductivity and temperature and the possibility to estimate activation energy from Eq. (1), the fitted equation tends to the value of  $0.22 \text{ S cm}^{-1}$  at high temperature, which is in agreement with the value reported by Zawodzinski et al. [25] of  $0.19 \text{ S cm}^{-1}$  at  $90^\circ\text{C}$ .

### 3.2. AFM study

The main advantage of the scanning probe microscopy compared with electron microscopy is the possibility to study samples under ambient conditions without any further preparation or restrictions. Samples in dry or wet states can be investigated in air. Topography images of Nafion samples stored in the different solvents are shown in Fig. 3. There is a large difference in topography between samples stored in water and others stored in alcohols while there is no significant difference between images of samples stored in alcohols. The same features were observed using the both contact mode and tapping mode. For example, images of samples in water and methanol in Fig. 3 were taken in contact mode

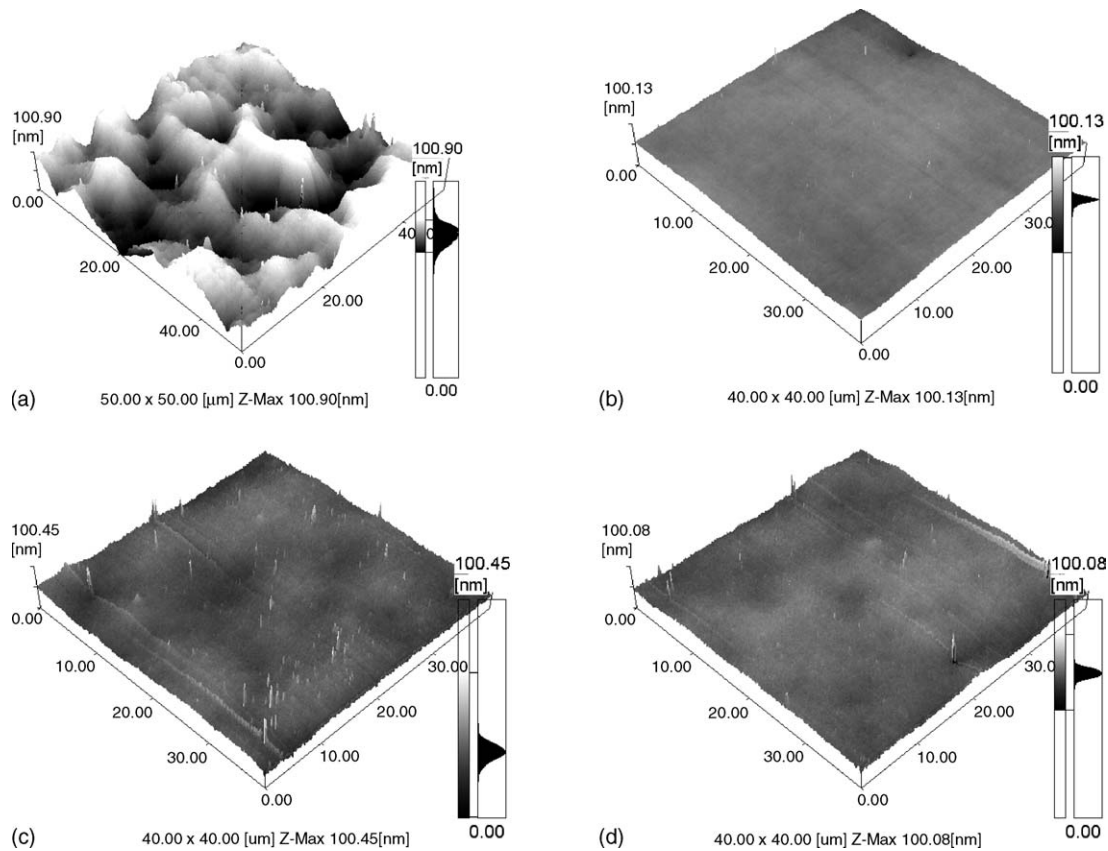


Fig. 3. AFM height images. Images (a), (b), (c) and (d) correspond to the topography of Nafion surface stored in pure water, methanol, ethanol and 2-propanol respectively. Water and methanol images are contact mode while ethanol and 2-propanol are tapping mode. Tapping mode images for water and methanol samples are shown in Fig. 4.

while those in Fig. 4 were taken in the tapping mode. We have also verified that the as-received samples without any pre-treatment when observed by AFM generally had the same roughness as the samples stored in water. Pre-treated samples subsequently observed in AFM also had the same roughness. However, samples dried in vacuum oven at 130 °C for 1 h had smooth surfaces. This indicates that pre-treatment itself under boiling conditions is not directly responsible for the observed features but the absorption and interaction of water with Nafion surface is the main reason for that because when water is removed either by drying in oven or removed by alcohols, especially methanol, the features disappeared. The surface water layer which probably formed on the surface of the sample, and tip convolution can both influence the image and result an image that does not truly reflect all the surface's features. However, it is unlikely that contributions of these phenomena are the only ones responsible for the shape of the features in the images obtained. The quantitative analysis of the roughness parameters is presented in Table 2 including the values of the arithmetic mean value  $R_a$  and root mean square (r.m.s.) parameters, which are typically used to quantify roughness in surface analysis. The comparison shows that roughness of Nafion in water is several times higher than in alcohols.

Fig. 4 shows the tapping mode AFM topography and phase images acquired simultaneously of Nafion previously immersed in water and methanol. This figure reveals that the topographic features observed with water immersion for the height images are not reproduced in the phase images. It is well known that material properties should affect the magnitude of the phase-shift signal and phase contrast can be used to distinguish between different materials on the surface. The features observed in the height images did not produce a strong phase-shift signal, indicating that phase contrast does not depend on the roughness of the surface. It also indicates that the roughness is related to the membrane material and not related to other foreigner materials. Comparison between the phase images acquired in water and methanol indicates that the surface structure of membrane is not affected by the roughness observed in the topographic images.

Table 2  
Roughness parameters and volume increase for different Nafion samples

Solvent	$R_a$ (nm)	R.m.s. (nm)	Volume increase $\Delta V/V$ (%) <sup>25</sup>
Water	26.772	32.595	43
Methanol	3.052	4.059	209
Ethanol	4.571	5.831	181
2-Propanol	4.736	6.214	114



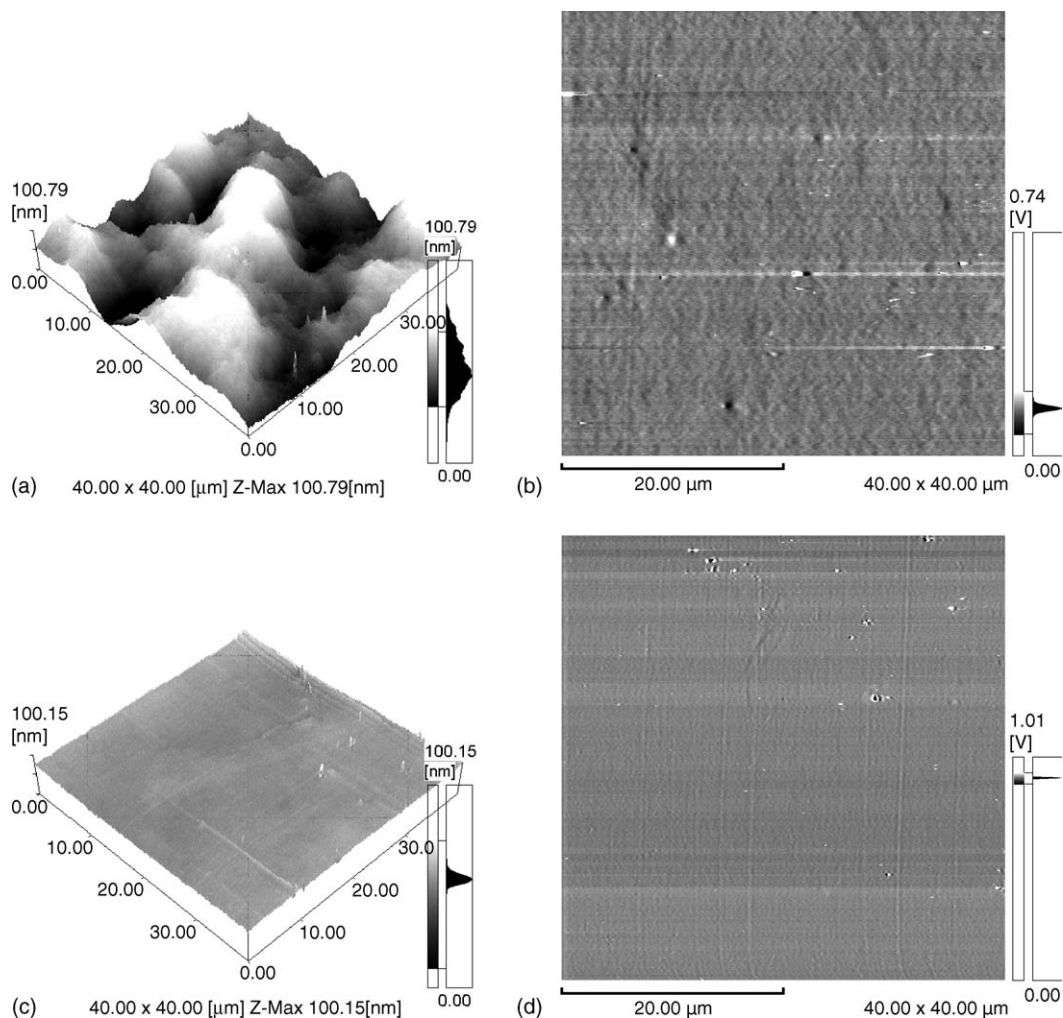


Fig. 4. AFM topography and corresponding phase image of Nafion samples stored in water (a, b) and methanol (c, d) respectively.

It is known that Nafion membrane absorbs water and other solvents and consequently expands to large dimensions [26,27]. Gebel et al. [26] first dried Nafion samples at 110 °C and then soaked them in numerous solvents. After that they measured the expansion of Nafion in the different solvents and found that in alcohols the membrane expands considerably more than in water as shown in Table 2. Litt [27] indicated that as more water is absorbed, it pushes the non polar domains further apart and expansion is restricted by the tie molecules that connect the domains. Elliot et al. [28] reported from SAXS study of swelling Nafion by ethanol–water mixtures that a less polar solvent than water can affect the behavior of fluorocarbon matrix. Yeo [17] also reported that solvent uptakes for Nafion are 21, 54, 50 and 58% in water, methanol, ethanol and 2-propanol, respectively. From these uptakes one can find by calculation that the volume increase is approximately 42, 136, 127 and 148% in water, methanol, ethanol and 2-propanol, respectively.

The volume increase,  $\Delta V/V$ , is the ratio between the volume of the solvent uptaken by the membrane and the volume of Nafion. It can be calculated, knowing the densities,  $\rho$ , of

Nafion and solvents, using the following equation:

$$\begin{aligned} \Delta V/V &= (m_{\text{Solvent}}/\rho_{\text{Solvent}})/(m_{\text{Nafion}}/\rho_{\text{Nafion}}) \\ &= \text{solvent uptake} \times (\rho_{\text{Nafion}}/\rho_{\text{Solvent}}) \end{aligned} \quad (5)$$

The densities of Nafion, water, methanol, ethanol and 2-propanol used in the calculation are 2, 1, 0.791, 0.789 and 0.785, respectively.

Yeo and Chen [18] showed that there is no significant difference in the behavior of Nafion H and Li forms versus the solvent uptakes. For H form, the uptakes are 21, 54 and 50% in water, methanol and ethanol respectively. For Li form, the uptakes are about 22, 48 and 46% in water, methanol and ethanol respectively. This indicated that comparison between Gebel and our results is possible because Gebel did experiments with Nafion Li form. However we did experiments with Nafion H form.

Comparatively with Gebel's experimental values, this indicates that Nafion structure undergoes high modification due to the swelling of the methanol. Our samples are pre-treated before being stored in methanol, so their surfaces are already

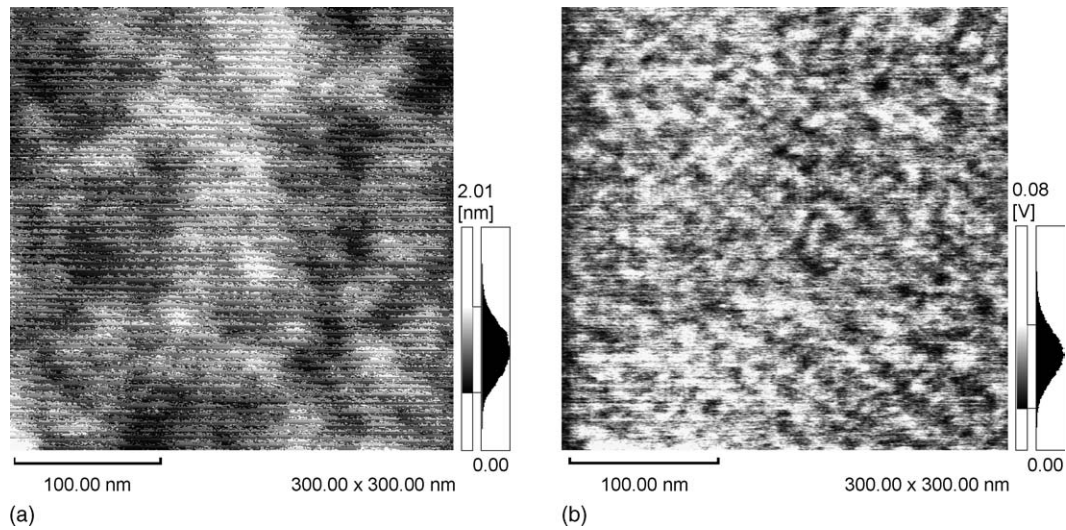


Fig. 5. High magnification AFM topography (a) and corresponding phase image (b) of Nafion samples stored in water.

rough before introducing them in the solvent. During equilibration, water is removed and replaced by methanol. All the material phases absorb the solvent which makes Nafion expand much more than in water. The expansion, for one direction, is almost homogenous because both fluorocarbon

matrix and ionic clusters interact with methanol and consequently the surface remains flat as for dry samples. When samples absorb water, the absorption of fluorocarbon matrix is less than that of ionic clusters and consequently the expansion, for one direction, is not homogenous and the surface

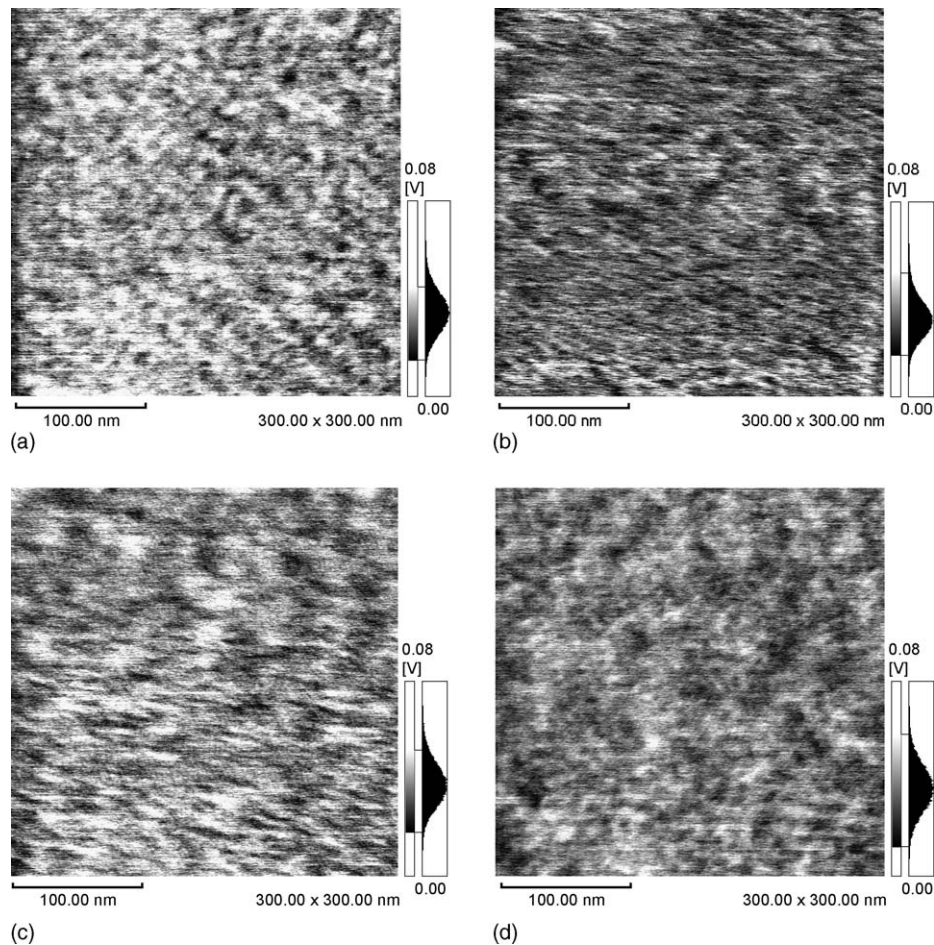


Fig. 6. High magnification AFM phase image of Nafion samples stored in water (a), methanol (b), ethanol (c) and 2-propanol (d).

does not remain flat. Therefore our AFM topography images clearly reflect the interaction between methanol and Nafion leading to the expansion of the bulk and the flatness of the surfaces. The same argument could be applied for results obtained with ethanol. However for 2-propanol, the calculated value of volume increase is higher than Gebel's experimental one. We attribute such divergence to two main reasons. First, it seems that 2-propanol and with less degree ethanol don't remove all water previously absorbed by Nafion. Topographic images (Fig. 3) clearly show that surfaces contours in 2-propanol and ethanol are in some extent resemble to that in water with bright and dark islands. This resemblance indicates that membrane is not fully dehydrated like with methanol. Second reason, we did not take in consideration in our calculation any structural change, which certainly affects the volume increase. In conclusion, Nafion absorbs alcohols more than in water and consequently expands much more according to Gebel and Yeo results. Surface modification observed by AFM is consistent with their reports.

Very high magnification images of samples stored in water are presented in Fig. 5. These images are found independent on the height area. This means that same images could be obtained from either higher or lower zones in topographic images, which reconfirms that the surface structure is not affected by roughness due to the absorption of water. Other authors who studied phase images for Nafion 115 acid form [10,11] and Nafion 117 potassium form [6] concluded that bright spots in very high magnification phase images are attributed to ionic clusters and dark spots correspond to fluorocarbon domains because the intensity of bright spots are dependent on water content. The average size of ionic clusters (Fig. 5(b)) is approximately 7–15 nm, which is in good agreement with data reported by McLean et al. [6].

Phase images in Fig. 6 correspond to samples stored in the different solvents. In the phase image corresponding to samples stored in methanol (Fig. 6(b)), ionic clusters and fluorocarbon domains can be also distinguished as in the case of water image. The shape of the ionic domain as well as the intensity of the phase signal in the methanol image is slightly different from those in the water image. These observations may support the recent report of Rivin et al. [29] in which indicates that water interacts more strongly with the sulfonic acid groups, while the alcohols preferentially solvate the fluoroether side chain and cause structural change. It seems that the phase image of methanol is consistent with this report and may indicate the absorption of methanol in the interfacial region of Nafion. Image corresponding to 2-propanol shows more defined clusters rather than images in methanol and ethanol. It also confirmed that 2-propanol does not fully dehydrate Nafion.

#### 4. Conclusions

It was established that both conductivity and surface topography of Nafion undergo high modification

when the membrane is transferred from water to alcohol environments.

Proton conductivity of Nafion membrane decreases in polar lower alcohols and correlates well with the dielectric constant of pure solvents and water–alcohol mixtures. The correlation has been explained on the basis of Born and Arrhenius equations. Nafion topography considerably changes when samples absorb water. However, samples stored in alcohols are characterized by flat surfaces. Surface modification was linked to expansion phenomenon and a swelling mechanism of Nafion in solvents. The interaction between the Nafion surface and methanol is different from that with water which is due to the presence of hydrophilic and hydrophobic zones in the Nafion structure. It seems that methanol cannot only remove and replace water but may also interact with perfluorinated vinyl ether chains.

The present study provided new data on the electrical and surface properties of the Nafion membrane. In situ electrochemical AFM allows the observation of surface property changes in an electrochemical environment. Our conclusions would be very useful in investigating alcohol oxidation in more detail by in situ electrochemical AFM using the tip as an electrode to obtain an electrical response during imaging of the Nafion membrane.

#### Acknowledgment

The present work was financially supported by the research and development of polymer electrolyte fuel cell from the New Energy and Industrial Technology Development Organization (NEDO), Japan.

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