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Morphology and properties of Nafion membranes prepared by solution casting

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ABSTRACT

In this study, dilute Nafion solutions consisting of solvents with various dielectric constants ε and solubility parameters δ, i.e. *N*,*N*′-dimethyl acetamide, *N*,*N*′-dimethyl formamide, *N*-methyl formamide, methanol–water mixture (4/1 g/g), ethanol–water mixture (4/1 g/g), and isopropanol–water mixture (4/1 g/g), were freeze dried and the conformations of Nafion molecules in dilute solutions were observed using transmission electron microscope. The membranes were prepared by solution casting from these solutions and evaporating the solvents at temperatures below T_G of Nafion, then annealing the membranes at 150 °C which was ~50 °C above T_G of Nafion. We show Nafion molecular conformations in dilute solutions are strongly influenced by δ and ε of solvents. And, thus the morphology, water uptake, proton conductivity, and methanol permeability of membranes prepared by solution casting are also influenced by δ and ε of solvents.

1. Introduction

Nafion is an ionomer produced by Du Pont Co. Its chemical structure consists of a perfluorocarbon backbone and vinylether side chains terminated with sulfonic acid groups [1,2]. The two chemical compositions of Nafion, i.e. hydrophobic perfluorocarbon backbone and hydrophilic sulfonated vinylether side chains, are incompatible. Yeo [3], using swelling method, determined the cohesive energy density of Nafion membrane and showed dual solubility parameters δ, i.e. $\delta_1 = 9.7\ (\text{cal/cm}^3)^{1/2}$ ascribed to the perfluorocarbon backbone and $\delta_2 = 17.3\ (\text{cal/cm}^3)^{1/2}$ ascribed to the sulfonated vinylether side chains. Nafion membranes have unique properties with respect to stability, solubility, and ionic conductivity, which make them suitable for a variety of applications [4]. It is an indispensable part for the proton exchange membrane (PEM) of proton exchange membrane fuel cells (PEMFCs). Besides its application as the PEM, the core part of PEMFC to separate fuel and oxidant, Nafion is also used in solution form for preparing membrane-electrode assembly (MEA), a fuel cell electrode for transporting both ions and electrons [5,6]. An important step in the modification of Nafion membranes is the recast process, in which a film is formed after evaporating the solvent from an ionomer solution. The solution casting film is of great interest in order to repair pin holes in Nafion chlor–alkali membranes [2] or for coating of modified electrodes [7]. The detailed procedure for preparing membranes from various solvents had been reported in literature [8–11].

Several studies have been devoted to the properties of Nafion solutions. Aldebert et al. [12], using Ubbelohde viscosity measurements, studied the Nafion solution properties with solvents of various dielectric constants. With aliphatic alcohols as solvents, Aldebert et al. showed polyeletrolyte effect of Nafion solutions increased with increasing dielectric constant of alcohols. The structures of Nafion molecules in water and aliphatic alcohols had been investigated using small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) for Nafion concentrations ranging from 5 to 20 wt%, and using electron spin resonance (ESR) for Nafion concentrations ranging from 1 to 22 wt% [12–17]. These experimental results revealed Nafion perfluorocarbon backbones aggregated and formed compact cylinders in solvents with sulfonated vinylether side chains surrounding on the surfaces of the aggregate cylinders and the sulfonated vinylether side chains were in contact with solvents. Dynamic light scattering (DLS) experiments were carried out in 10 mg/ml Nafion/ethanol–water (50/50 vol ratio) [18], 5.3 mg/ml Nafion/water [19], and 0.2–9.0 mg/ml Nafion/methanol–water (methanol/water = 4/1 g/g) solutions

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[20]. Two different sizes of Nafion aggregate particles were found as Nafion concentration was above 5 mg/ml in water, methanol, and ethanol solvents. These authors attributed these two aggregates to the hydrophobic interaction of fluorocarbon backbones and the electrostatic interaction of sulfonic acid ion pairs of vinylether side chains. Static light scattering (SLS) experiments from dilute *N*, *N*′-dimethyl acetamide (DMAc) and *N*,*N*′-dimethyl formamide (DMF) solutions were also carried out to measure Nafion molecular weight [21].

In literature the structure of Nafion membranes is most often investigated using small-angle scattering [22–33], wide angle X-ray diffraction [23,33,34], atomic force microscope [35–37], and electron microscope [38]. Several models regarding the structure of the organization of the ionic groups had been proposed. One of the most attention models is the cluster model. The theoretical approach to cluster model of organic ionomers was first proposed by Eisenberg et al. [39,40]. Marx et al. [41] introduced cluster model to explain the behavior in hydrocarbon ionomers, such as poly (ethylene methacrylic acid) and poly(butadiene methacrylic acid) copolymers. Similar ionic cluster behavior was also proposed latter by Roche et al. [22] and Gierke et al. [23]. The cluster model suggests the electrostatic interactions hold the ionic groups in regions with spherical shape and in the order of several nanometers in size. These spherical ionic clusters are connected by small channels and thus protons can travel from one ionic cluster to another.

Though the morphology of Nafion membranes had been reported in literature, however, most of the researchers studied the membranes directly obtained from Du Pont Co. Few papers reported morphology of Nafion membranes prepared by solution casting and the influence of solvents on the properties of membranes. The dual solubility parameters of perfluorocarbon backbones and sulfonated vinylether side chains and the ionic property of side chain sulfonic acid groups lead Nafion molecular conformations to strongly depend on the solubility parameter δ and dielectric constant ε of solvents. In this study, using freeze drying technique and transmission electron microscope (TEM), we report conformations of Nafion molecules in dilute solutions with solvents of various ε and δ, i.e. DMAc, DMF, *N*-methyl formamide (NMF), methanol/water (MeOH–H_2O, 4/1 g/g) mixture, ethanol/water (EtOH–H_2O, 4/1 g/g) mixture, and isopropanol/water (IPA–H_2O, 4/1 g/g) mixture solvents. The Nafion membranes were prepared by solution casting from these solvents and evaporating the solvents at temperatures below T_G of Nafion, then annealed the membranes at 150 °C under vacuum for 90 min. Because of high boiling points of DMAc ($T_b = \sim 165$ °C) and NMF ($T_b = \sim 198$ °C) solvents, annealing membranes at high temperature, i.e. 150 °C, under vacuum is easier to reduce residual solvents remained in the membranes. Each membrane was then separated into two pieces with one piece of the membranes stored in a container at 25 °C with a relative humidity (RH) of 37% and the other piece of the membranes stored at 25 °C in distilled water. The morphology of these membranes were observed using small-angle X-ray scattering (SAXS) and differential scanning calorimetric (DSC) analysis. The water uptake, proton conductivity, and methanol permeability are the most important properties of PEMs and are the key factors controlling the PEMFC and DMFC (direct methanol fuel cells) performances. In this study, we also investigated water uptake, proton conductivity, and methanol permeability of Nafion membranes prepared by solution casting. We show the morphology and thus the water uptake, proton conductivity, and methanol permeability of Nafion membranes prepared by solution casting are strongly influenced by the solvents. The influences of solvents on the conformations of Nafion molecules in dilute solutions and morphology and properties of membranes prepared by solution casting were discussed based on δ and ε of solvents. Most of the commercialized Nafion membranes are annealed at a temperature around 120–130 °C. In order to compare the properties of membranes prepared by solution casting with those of commercial membranes, we also carried out water uptake, proton conductivity, and methanol permeability measurements on the membranes prepared by solution casting and annealed at 125 °C for 90 min and stored at 25 °C in distilled water. Small amount of residual high boiling point solvents might remain in the membranes prepared from DMAc and NMF solutions. But the measured data were still acceptable.

2. Experimental section

2.1. TEM observations of Nafion conformations in dilute solutions

The solvent of as-received 5 wt% Nafion solution (Du Pont Co, EW = 1100, the solvent was a mixture of water, methanol, isopropanol, and unspecified mixed ether) was evaporated at 60 °C under vacuum for 1 h to obtain a solid resin. The solid Nafion resin was then dissolved in DMAc, DMF, NMF, MeOH–H_2O (4/1 g/g), EtOH–H_2O (4/1 g/g), and IPA–H_2O (4/1 g/g) solvents to prepare 0.6 mg/ml Nafion solutions. A copper grid with 400 mesh carbon film (CF400-Cu, Electron Microscopy Sciences, Inc., PA) was floated on the top of the surface of a drop of 0.6 mg/ml Nafion solution for 12 h. Thus a thin film of Nafion solution was covered on the surface of the copper grid. The copper grid with a thin film of a Nafion solution was frozen immediately in a liquid nitrogen container at a temperature of approximately −190 °C for 4 h. The solvent of the frozen Nafion thin film on the copper grid surface was dried under vacuum at −130 °C for 5 h. The copper grid with a dried Nafion film on its surface was then immersed in 0.5 M $Pb(NO_3)_2$ (Aldrich Chemical Co) aqueous solution for 5 min to stain the sulfonic acid groups of Nafion, and then dried at room temperature. The copper grid was then rinsed with deionized water and dried at room temperature. TEM observations were performed on a Hitachi model 7500 TEM at an accelerating voltage of 75 kV. The thickness of the Nafion thin film on a TEM copper grid was around ~70 nm. The Nafion thin film thickness was estimated from the weight of Nafion coated on a copper grid, the surface area of a copper grid (diameter = 1.5 mm), and the density of solid Nafion (density = 2.10 g/cm^3 [27]). The weight of Nafion thin film coated on a copper grid was measured by subtracting weight of 100 empty copper grids from the weight of 100 copper grids coated with Nafion thin films.

2.2. Preparations of Nafion membranes

The Nafion solutions prepared in Experimental section 2.1 were cast in glass vessels and the solvents were evaporated at 50 °C (which is below $T_G = 100$ °C of Nafion) for 30 h, then under vacuum at 80 °C for another 1 h. Two pieces of membranes were prepared and annealed under vacuum at 125 °C and 150 °C for 90 min. Each membrane was separated into two pieces with one piece of membrane being stored at 25 °C in a container with 37% RH and the other piece of membrane being stored in distilled water at room temperature. TGA, DSC, SAXS, proton conductivity, and methanol permeability investigations were carried out on the membranes annealed at 150 °C. However, only TGA, proton conductivity, and methanol permeability measurements were carried out for membranes annealed at 125 °C. The membranes were stored at least for one week to reach equilibrium before TGA, DSC, SAXS, proton conductivity, and methanol permeability investigations.

2.3. Thermogravimetric analysis (TGA)

TGA observations of membranes were performed under N_2 on a Thermal Analysis (TA) Model Q50 TGA. The samples sizes were around 5–10 mg. Before TGA observations, the surface of each sample was dried with lens papers to clean the residual water on the surface of the membrane. The heating rate was 5 °C/min and the N_2 flow rate was 20 ml/min.

2.4. Differential scanning calorimetry (DSC)

DSC experiments of membranes were performed on a Thermal Analysis Model Q10 DSC. The sample sizes were 5–10 mg. Before DSC observations, the surface of each sample was dried with lens paper to clean the water on the surface of membrane. The heating rate was 10 °C/min and the N_2 flow rate was 20 ml/min.

2.5. Small-angle X-ray scattering (SAXS)

SAXS of Nafion membranes were performed at the BL17B3 SWAXS endstation of the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan [42]. With a beam of 0.5 mm dia. and a sample-to-detector distance of 1.25 m, SAXS data were collected with 1.24 Å X-rays using a gas-type area detector. The polyethylene (PE) was used as a standard to obtain the absolute scattering intensity. Each SAXS spectrum was collected for 20 min at 25 °C. The thickness of each sample was around ~50 μm.

2.6. Conductivity measurement

The ionic conductivity (σ) of membranes was calculated from the measured resistance (r) using Eq. (1):

$$\sigma = d/(a \times r) \tag{1}$$

where a is the cross section area of membrane for a resistance measurement and d the thickness of a membrane. r was measured using an ac impedance system (model SA1125B, Solartron Co, UK). The membranes prepared as described in Section 2.2 and stored at 25 °C in distilled water were used for conductivity measurements. Before r measurements, the membrane was immersed in 0.5 M H_2SO_4 aqueous solution at 85 °C (85 °C < T_G of Nafion) for 1 h and then immersed in distilled water at room temperature for 10 min to clean the residual H_2SO_4 on the surface of the membrane. A device capable of holding a membrane for r measurement was located between probes. The testing device with a membrane was kept in a thermo-stat under a relative humidity (RH) of 95% and a temperature of 70 °C. The membrane area a for r measurement was $a = 3.14\ \text{cm}^2$.

2.7. Methanol permeability measurement

Methanol permeability of membranes was investigated using an apparatus designed by our lab. The membranes prepared as described in Section 2.2 and stored at 25 °C in distilled water were used for methanol permeability P measurements. A device of holding a membrane was located in the middle of two vessels, with each vessel having a volume of 400 cm^3. At the beginning of methanol permeability test, the source vessel-a was filled with 9.86 wt% methanol aqueous solution and the receiving vessel-b was filled with pure distilled water. The whole apparatus was kept at a constant temperature. After methanol crossover the membrane for a measuring time t, 2 ml of liquid was taken from vessel-b and its density was measured using a density meter (DA-505, KEM, Japan). The concentration of methanol ($C_b(t)$) of the receiving vessel-b at a methanol crossover measurement time t was then calculated using a standard calibration curve, which was a plot of measured liquid density data versus methanol concentration of methanol aqueous solutions with known methanol concentrations. The methanol permeability measurements of each membrane were carried out at 30 °C and 70 °C for 10 h. During the methanol crossover experiment, the methanol concentration $C_b(t)$ of receiving vessel-b was measured at a time interval of 3600 s. The methanol permeability P of a membrane was obtained from the slope of the plot of $C_b(t)$ versus t of Eq. (2) [43]:

$$C_b(t) = t \times C_a \times [(P \times A)/(d \times V_b)] \tag{2}$$

In Eq. (2), C_a is the wt ratio of methanol in methanol aqueous solution (g-methanol/g-solution) in source vessel-a, t (in unit of seconds) the time of methanol crossover measurement, A the cross section area of membrane for methanol crossover measurement, d the thickness of membrane, and V_b the volume of receiving vessel-b. In this study, $C_a = 0.0986$ g/g, $A = 4.90\ \text{cm}^2$, and $V_b = 400\ \text{cm}^3$.

3. Results and discussion

3.1. Solubility parameters and dielectric constants

The solubility parameters and dielectric constants of solvents [44,45] and dual solubility parameters of Nafion obtained from Yeo [3] are summarized in Table 1. In Table 1, we also list the δ and ε of MeOH–H_2O (4/1 g/g), EtOH–H_2O (4/1 g/g), and IPA–H_2O (4/1 g/g) mixture solvents, which were calculated using Eqs. (3) and (4), respectively [45]:

$$\delta_m = [E_{coh,m}/V_m]^{1/2} = \left[\left(\sum X_i E_{coh,i}\right)/\left(\sum X_i V_i\right)\right]^{1/2} \tag{3}$$

$$\rho_m = \sum X_i \rho_i = \sum X_i \varepsilon_i^{1/2} M_i \tag{4a}$$

$$\varepsilon_m = \left[\rho_m/\left(\sum X_i M_i\right)\right]^2 \tag{4b}$$

In Eqs. (3) and (4), δ_m is the solubility parameter of the mixture solvent, $E_{coh,m}$ the cohesive energy of the mixture solvent, V_m the molar volume of the mixture solvent, X_i the molar ratio of solvent-i, $E_{coh,i}$ the cohesive energy of solvent-i, V_i the molar volume of solvent-i, ρ_m the molar dielectric polarization of a mixture solvent, ρ_i the molar dielectric polarization of solvent-i, ε_m the dielectric constant of a mixture solvent, ε_i the dielectric of solvent-i, and M_i the molecular weight of solvent-i.

Table 1
Solubility parameters and dielectric constants of solvents and Nafion.

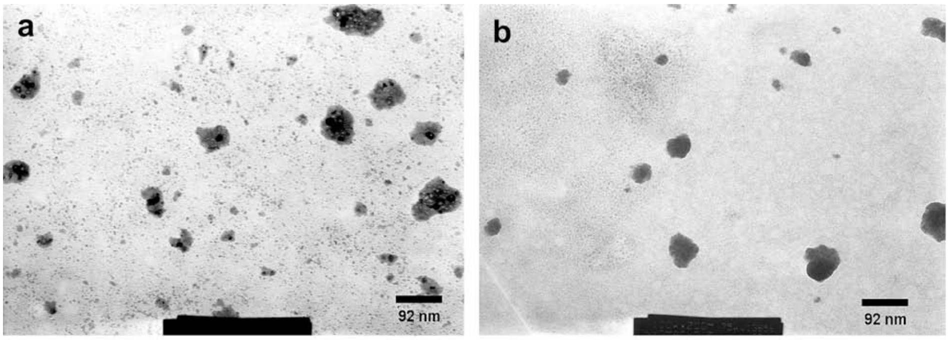
Solvent	δ $(\text{cal/cm}^3)^{1/2}$	ε
Water	23.4	78.4
Methanol	14.5	32.7
Ethanol	12.7	24.5
Isopropanol	11.8	19.9
Methanol–water (4/1 g/g)	16.3[a]	40.3[b]
Ethanol–water (4/1 g/g)	15.0[a]	32.2[b]
Isopropanol–water (4/1 g/g)	14.4[a]	28.5[b]
NMF	16.1	182.4
DMF	12.2	36.7
DMAc	10.8	37.8
Nafion[c]	9.7, 17.3	–

[a] Calculated using Eq. (3).
[b] Calculated using Eqs. (4a) and (4b).
[c] Ref. [3].

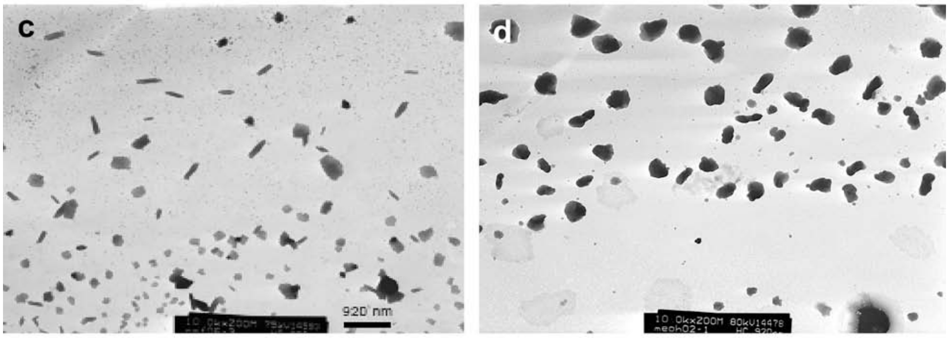
3.2. TEM observations of Nafion conformations in dilute solutions

Fig. 1a–f shows TEM micrographs of polymer chain conformations of 0.6 mg/ml Nafion in DMAc, DMF, NMF, MeOH–H_2O, EtOH–H_2O, and IPA–H_2O solutions, respectively, after freeze drying. Liu et al. [21] carried out static light scattering (SLS) from Nafion/DMAc and Nafion/DMF solutions with Nafion concentrations ranging from 0.2 mg/ml to 1.0 mg/ml. They obtained $\langle M_w \rangle = 2.58 \times 10^5$ g/mol and $\langle R_G \rangle = 36.5$ nm from Nafion/DMAc solutions and $\langle M_w \rangle = 2.55 \times 10^5$ g/mol and $\langle R_G \rangle = 22.2$ nm from Nafion/DMF solutions. These results were consistent with the $\langle M_w \rangle = 2.50 \times 10^5$ g/mol obtained from dilute Nafion/DMSO (dimethyl sulfoxide) solutions obtained by Lousenberg [46] using a size exclusion chromatography incorporating static light scattering. Liu et al. and Lousenberg $\langle M_w \rangle$ data were close to those reported by Alderbert et al. [13]. Alderbert et al. mentioned $M_w \sim 2.0 \times 10^5$ g/mol of Nafion (EW = 1100), which was obtained from a personal communication with Du Pont Co. Using the SLS $\langle R_G \rangle$ data and the equation of overlap concentration $C^* = 3\langle M_w \langle/(4\pi\langle R_G\langle^3 N_A)$ (where N_A is Avogadro number), we obtained $C^* = 2.1$ mg/ml and 9.4 mg/ml for Nafion in DMAc and DMF solutions, respectively. From the above mentioned results, we may conclude that the Nafion concentration of 0.6 mg/ml of present study was below C^*. The conformation of Nafion molecules does not change much near this concentration. We may also conclude that Nafion molecules form single chained structures in the present 0.6 mg/ml DMAc and DMF solutions. The micrographs of Fig. 1a–f show that Nafion molecules have sphere-like structures in DMF and DMAc solvents, mixture of thin rod-like and rectangle-like structures in NMF, mixture of rectangle-like (or thick rod-like) and cube-like structures in MeOH–H_2O solvent, mixture of rod-like and rectangle-like structures in EtOH–H_2O solvent, and mixture of rectangle-like and cube-like structures in IPA–H_2O solvent.

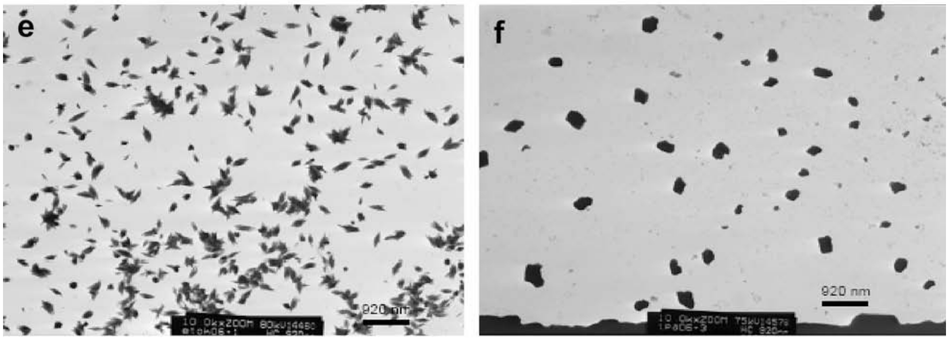
The various conformations of Nafion molecules in different solvents can be explained using δ and ε of solvents. The solubility parameters of Nafion are $\delta_1 = 9.7$ $(cal/cm^3)^{1/2}$ and $\delta_2 = 17.3$ $(cal/cm^3)^{1/2}$ relating to perfluorocarbon backbone and vinylether sulfonic acid side chains, respectively. From Table 1, we know that $\delta = 10.8$ $(cal/cm^3)^{1/2}$ of DMAc and $\delta = 12.2$ $(cal/cm^3)^{1/2}$ of DMF are



DMAc ($\times10^5$; — 92 nm) DMF ($\times10^5$; — 92 nm)



NMF ($\times10^4$; — 920 nm) MeOH-H_2O ($\times10^4$; — 920 nm)



EtOH-H_2O ($\times10^4$; — 920 nm) IPA-H_2O ($\times10^4$; — 920 nm)

Fig. 1. TEM micrographs of 0.6 mg/ml Nafion solutions after freeze drying. Solvents: (a) DMAc; (b) DMF; (c) NMF; (d) MeOH–H_2O; (e) EtOH–H_2O; (f) IPA–H_2O.

close to the δ_1 of perfluorocarbon backbones and far from the δ_2 of vinylether sulfonic acid side chains of Nafion. The solvents DMAC and DMF are more compatible with perfluorocarbon backbones and not compatible with vinylether side chains of Nafion. Thus few perfluorocarbon backbones of Nafion molecules aggregate in DMAc and DMF solvents. Nafion molecules form single chain coiled structures in dilute DMAc and DMF solutions (Fig. 1a and b). The vinylether sulfonic acid side chains are buried inside the coils and the perfluorocarbon backbones are on the surfaces of coils and in contact with solvents of Nafion. Table 1 shows NMF has $\delta = 16.1$ (cal/cm^3)$^{1/2}$ and $\varepsilon = 182.4$. The δ of NMF is close to the δ_2 of vinylether side chains and far from the δ_1 of perfluorocarbon backbones of Nafion. NMF is compatible with vinylether side chains and not compatible with perfluorocarbon backbones. Thus Nafion perfluorocarbon backbones may aggregate in NMF with the vinylether side chains surrounding on the surfaces of aggregation particles and in contact with NMF solvent. Also the high ε of NMF causes high dissociations of sulfonic acid groups and formation of highly negative charges on side chain sulfonic acid groups. The electrostatic charge repulsions among the highly negative charged side chains cause Nafion molecules to form rod structures. Nafion molecules also form backbone aggregations in alcohol–water mixture solvents, which will be discussed in the next section. However, owing to the much higher ε of NMF than alcohol–water mixture solvents, the electrostatic charge repulsion among Nafion molecules in NMF is much larger than in alcohol–water mixture solvents. Thus the degree of perfluorocarbon backbone aggregations in NMF (Fig. 1c) is lower than in alcohol–water mixture solvents (Fig. 1d–f).

Szajdzinska-Pietek et al. [15,16] used electron spin resonance (ESR) to study Nafion molecular conformations in water and methanol solvents. Their experimental results revealed Nafion perfluorocarbon backbones aggregated and formed compact cylinders in water and methanol solvents with sulfonated vinylether side chains surrounding on the surfaces of the aggregate cylinders and the sulfonated vinylether side chains were in contact with water and methanol solvents. Those results are similar to the Nafion molecular conformations shown in TEM micrographs of Fig. 1d–f. Table 1 shows the δ of MeOH–H_2O is 16.3 (cal/cm^3)$^{1/2}$, which is close to the δ_2 of vinylether sulfonic acid side chains and far from the δ_1 of perfluorocarbon backbones of Nafion. Thus MeOH–H_2O solvent is more compatible with vinylether sulfonic acid side chains but not with perfluorocarbon backbones. Nafion backbones aggregate in MeOH–H_2O with vinylether side chains surrounding on the surfaces of particles and in contact with solvent. The high $\varepsilon = 40.3$ of MeOH–H_2O results in the formation of negative charges on Nafion molecules. The electrostatic charge repulsions among the negative charged side chains caused formation of anisomeric rod-shape conformations. The ε of MeOH–H_2O is lower than that of NMF. The inter-polymer electrostatic charge repulsions among the Nafion molecules in MeOH–H_2O solvent are lower than in NMF. More Nafion backbones aggregate in MeOH–water than in NMF and form rectangle-like and cube-like structures as shown in Fig. 1d. EtOH–H_2O and IPA–H_2O solvents have similar properties to MeOH–H_2O solvent. But comparing with MeOH–H_2O, the δs of EtOH–H_2O and IPA–H_2O are lower and closer to $\delta_1 = 9.7$ (cal/cm^3)$^{1/2}$ of Nafion perfluorocarbon backbones. Thus Nafion perfluorocarbon backbones are more compatible with EtOH–H_2O and IPA–H_2O than with MeOH–H_2O. Thus the degrees of Nafion perfluorocarbon backbone aggregations in EtOH–H_2O and IPA–H_2O are lower than in MeOH–H_2O as shown in Fig. 1d–f. Comparing Fig. 1e with Fig. 1f, we found the shapes of Nafion aggregated particles were thin and behaved as rod-like and rectangle-like structures in EtOH–H_2O and were thick and behaved as rectangle-like and cube-like structures in IPA–H_2O. The reasons for the different shape of Nafion molecules in these two solvents can be attributed to the lower δ and ε of IPA–H_2O than EtOH–H_2O. The lower δ of IPA–H_2O than EtOH–H_2O causes Nafion molecular backbones and are more compatible with IPA–H_2O than with EtOH–H_2O. The lower ε of IPA–H_2O than EtOH–H_2O causes less ionic –SO_3H dissociation of Nafion and lower negative charge repulsion of Nafion side chain sulfonic acid groups in IPA–H_2O than in EtOH–H_2O. Thus the Nafion molecular chains are more flexible and less stick in IPA–H_2O than in EtOH–H_2O and the shape of Nafion aggregated particles are thicker in IPA–H_2O than in EtOH–H_2O. The other reason for the thicker Nafion aggregated particles in IPA–H_2O than in EtOH–H_2O can be attributed to the different degrees of Nafion–$SO_3^-\cdots$HO–CH(CH_3)$_2$ interactions in IPA–H_2O solvent and Nafion–$SO_3^-\cdots$HO–C_2H_5 interactions in EtOH–H_2O solvent. Because of higher molecular weight of IPA than EtOH, the number of IPA molecules in IPA–H_2O (4/1 g/g, 1.2/1 mole/mole) is lower than that in EtOH–H_2O (4/1 g/g, 1.56/1 mole/mole). The frequency of Nafion–$SO_3^-\cdots$HO–CH(CH_3)$_2$ interactions in IPA–H_2O solvent is lower than that of Nafion–$SO_3^-\cdots$HO–C_2H_5 interactions in EtOH–H_2O solvent. The lower interaction frequency of Nafion–SO_3H groups with IPA molecules than Nafion–SO_3H groups with EtOH molecules results in thicker Nafion aggregated particles in IPA–H_2O than in EtOH–H_2O.

Fig. 2 shows the cartoons of Nafion molecular chain conformations in 0.6 mg/ml dilute DMAc, DMF, NMF, MeOH–H_2O, EtOH–H_2O, and IPA–H_2O solutions. Nafion molecules form single chain coiled structures in DMAc and DMF solvents. Nafion perfluorocarbon backbones aggregate and form thin rod structures in NMF solvent, and mixture of rectangle-like and cube-like structures in MeOH–H_2O, EtOH–H_2O, and IPA–H_2O solvents with vinylether sulfonic acid side chains located on the surfaces of rods and in contact with solvents. The sizes of aggregated Nafion particles in solvents decrease sequentially as following: MeOH–$H_2O > $ EtOH–$H_2O \sim$ IPA–$H_2O >$ NMF $>$ DMAc $\sim$ DMF.

When membranes were prepared by solution casting and evaporating the solvents at temperatures below T_G, the conformations of Nafion molecules in solutions would be remained in the membranes after solvents were evaporated. Nafion molecules may have similar conformations as in dilute solutions and the aggregated/or coiled particles are close and overlap with each other. After the membrane was annealed at a temperature above T_G, the local segmental motion could induce further aggregation and caused more compact and order packing of perfluorocarbon backbones. But the global morphology of membranes was inherited from the chain conformations in solutions before annealing. Fig. 3 shows the cartoons of the morphology of Nafion thin layers after evaporation of solvents before annealing. The real membranes are overlaps of lots of thin layers. In Fig. 3, the long lines are Nafion backbones and the short branches attached on the long lines are ionic side chains, and the empty spaces surrounded by Nafion molecules with ionic side chains locating on the surfaces of empty spaces are ionic sulfonic acid group aggregation clusters.

As solvents were evaporated from cast solutions, Nafion side chain sulfonic acid groups will move along with perfluorocarbon backbones to form solid membranes. Thus larger backbone aggregations in membranes result in the formation of larger sulfonic acid group aggregations, i.e. larger ionic clusters. Because of low degree of backbone aggregations in dilute DMAc and DMF solutions, few perfluorocarbon backbone aggregations happen in membranes when membranes are prepared from DMAc and DMF solvents. Thus perfluorocarbon backbones and vinylether sulfonic acid side chains randomly distribute and overlap in the membranes with low degrees of perfluorocarbon backbone aggregations and ionic sulfonic acid group aggregations when membranes were prepared from DMAc and DMF. Because of highly negative charge repulsions

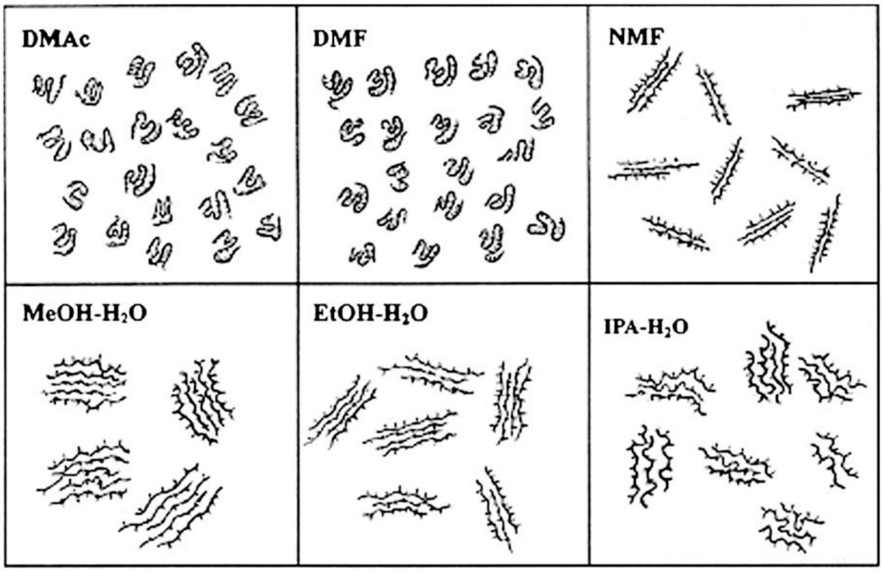


Fig. 2. Conformations of Nafion molecules in dilute solutions. Solvents, upper row: DMAc (left), DMF (middle), NMF (right); bottom row: MeOH–H_2O (left), EtOH–H_2O (middle), IPA–H_2O (right). The long lines indicate Nafion backbones and short branches attached on long lines indicate the ionic side chains.

among ionic side chains, the degree of Nafion backbone aggregation is low in dilute NMF solutions. The rod-like backbone aggregate particles randomly distribute in membranes after the solvent is evaporated from NMF solution. Because of larger perfluorocarbon backbone aggregations in alcohol–water solutions, the sizes of backbone aggregations and side chain sulfonic acid group aggregations are larger in membranes prepared from alcohol–water solvents than from DMAc, DMF, and NMF solvents. In Fig. 3, we show the sizes of ionic aggregations are smaller in membranes prepared from DMAc, DMF, and NMF solvents than those prepared from alcohol–water solvents. In Fig. 3, we also show the degree of backbone aggregations and the sizes of side chain sulfonic acid group aggregations decrease when the solvent for membrane preparations is varied from MeOH–H_2O to EtOH–H_2O and to IPA–H_2O, because the degree of backbone aggregations in solvents decreases following the sequence of MeOH–$H_2O >$ EtOH–$H_2O \sim$ IPA–H_2O.

Since the side chain sulfonic acid group aggregated clusters are the regions where water molecules locate in membranes after the membranes are swollen with water, the water uptake in membrane should be proportional to the degree and sizes of sulfonic acid group aggregations [23]. Gierke et al. [23] and Gebel [29] had shown the increase of water uptake in a membrane resulted in an increase in the number sulfonic acid groups of the aggregated clusters (see Fig. 18 of Ref. [23] and Fig. 7 of Ref. [29]). The water uptake of a membrane is an indicator of the degree of side chain sulfonic acid group aggregations. When ionic side chains and perfluorocarbon backbones distribute randomly in membranes,

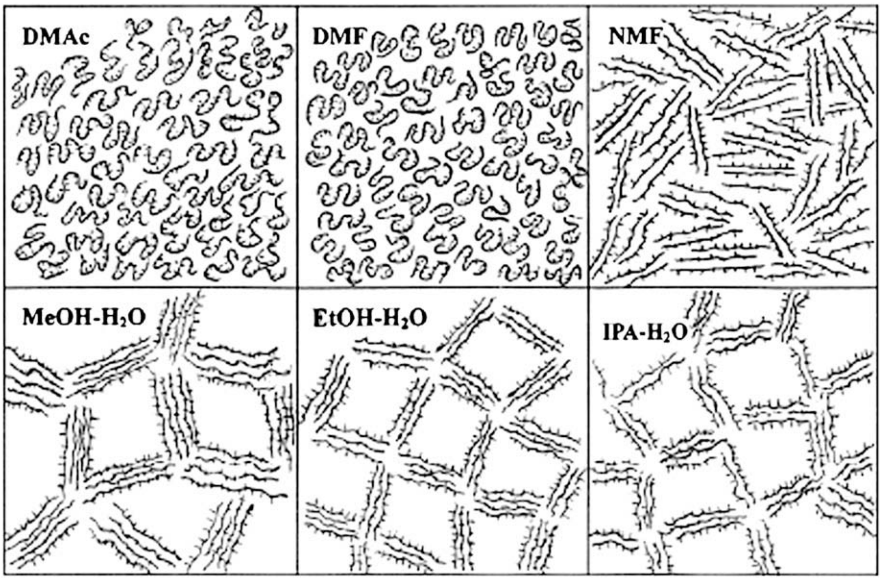


Fig. 3. Morphology of Nafion thin layers after solvents are evaporated from casting solutions. Solvents, upper row: DMAc (left), DMF (middle), NMF (right); bottom row: MeOH–H_2O (left), EtOH–H_2O (middle), IPA–H_2O (right). The long lines indicate Nafion backbones and short branches attached on long lines indicate ionic side chains. The empty spaces surrounded by Nafion molecules with ionic side chains located on the surfaces of empty spaces are ionic sulfonic acid group aggregation clusters.

few side chain sulfonic acid group aggregations and also few perfluorocarbon backbone aggregations form in membranes. Thus the membranes with low degree of backbone aggregations and low degree of sulfonic acid group aggregations should have low water uptake. However when large perfluorocarbon backbones aggregate in membranes, large phase separation between perfluorocarbon backbones and vinylether side chains happen in membranes, leading to the formation of large side chain sulfonic acid group aggregations and thus high water uptake of membranes.

The degree of backbone aggregations of Nafion membranes can be investigated using SAXS at a scattering vector of $q = 0.6–0.7\ \text{A}^{-1}$ and also using DSC by measuring the dissociation enthalpy of backbone aggregations. The degree and sizes of ionic sulfonic acid group aggregations can also be investigated using SAXS at a scattering vector of $q = 1.9–2.2\ \text{A}^{-1}$, using TGA by measuring the weight loss due to water evaporation at temperatures below 250 °C, and also using DSC by measuring the enthalpies of the dissociation of sulfonic acid group aggregations and water evaporation. In the following sections, we will investigate the membrane structures using TGA, DSC, and SAXS. We show that the experimental results were consistent with Nafion molecular chain structures shown in Fig. 3.

3.3. TGA study

Fig. 4a and b shows the TGA data of Nafion membranes stored at 25 °C with 37% RH and at 25 °C in distilled water, respectively, after they were annealed at 150 °C for 90 min. The weight loss at temperature below 250 °C is due to the evaporation of water. The weight loss around 270–360 °C can be attributed to the decomposition of side chain ether sulfonic acid groups. And, the weight loss at temperature above 400 °C is due to the decomposition of Nafion main chains [47]. Tables 2a and 2b summarize the water contents (weight loss below 250 °C) and 1st decomposition temperatures (decomposition of ether sulfonic acid groups) of membranes obtained from Fig. 4a and b, respectively. These results revealed that membranes prepared from alcohol–water mixture solvents had higher water content than those prepared from DMAc, DMF, and NMF solvents. These results are consistent with the cartoons shown in Figs. 2 and 3, which show low degrees of perfluorocarbon backbone aggregations and vinylether sulfonic acid group aggregations when membranes were prepared from DMAc, DMF, and NMF, and high degrees of perfluorocarbon backbone aggregations and vinylether sulfonic acid group aggregations when membranes were prepared from alcohol–water mixture solvents. Tables 2a and 2b also show that the water uptake of membranes decreased when the solvent used for preparing membranes varied from MeOH–H_2O to EtOH–H_2O and to IPA–H_2O. These results were consistent with the cartoons shown in Figs. 2 and 3. In Fig. 3, we show the degree of perfluorocarbon backbone aggregations and the sizes of side chain sulfonic acid group aggregations decrease when the solvent for membrane preparation is varied from MeOH–H_2O to EtOH–H_2O and to IPA–H_2O. Tables 2a and 2b show that membranes prepared from alcohol–water mixture solvents had lower 1st decomposition temperatures than those prepared from DMAc, DMF, and NMF solvents. In Section 3.5 (SAXS study), we will calculate the ratio n/N (where n is the number of –SO_3H groups located in an ionic aggregation site and N the total number of –SO_3H groups associated to an ionic aggregation site) of membranes prepared from various solvents. The n/N values of membranes stored at 25 °C with 37% RH and at 25 °C in distilled water are listed in Tables 6 and 7, respectively. Comparing Tables 2a and 2b with Tables 6 and 7, we found that the membranes prepared from alcohol–H_2O mixture solvents had higher n/N ratio and lower 1st decomposition temperature than those prepared from DMAc, DMF, and NMF solvents. These results indicate that –SO_3H groups located in ionic aggregation sites are easier to be decomposed than those mixed in perfluorocarbon backbone aggregation regions. Thus more sulfonic acid groups join the ionic aggregation sites (i.e. higher n/N value) and resulted in a lower 1st decomposition temperature.

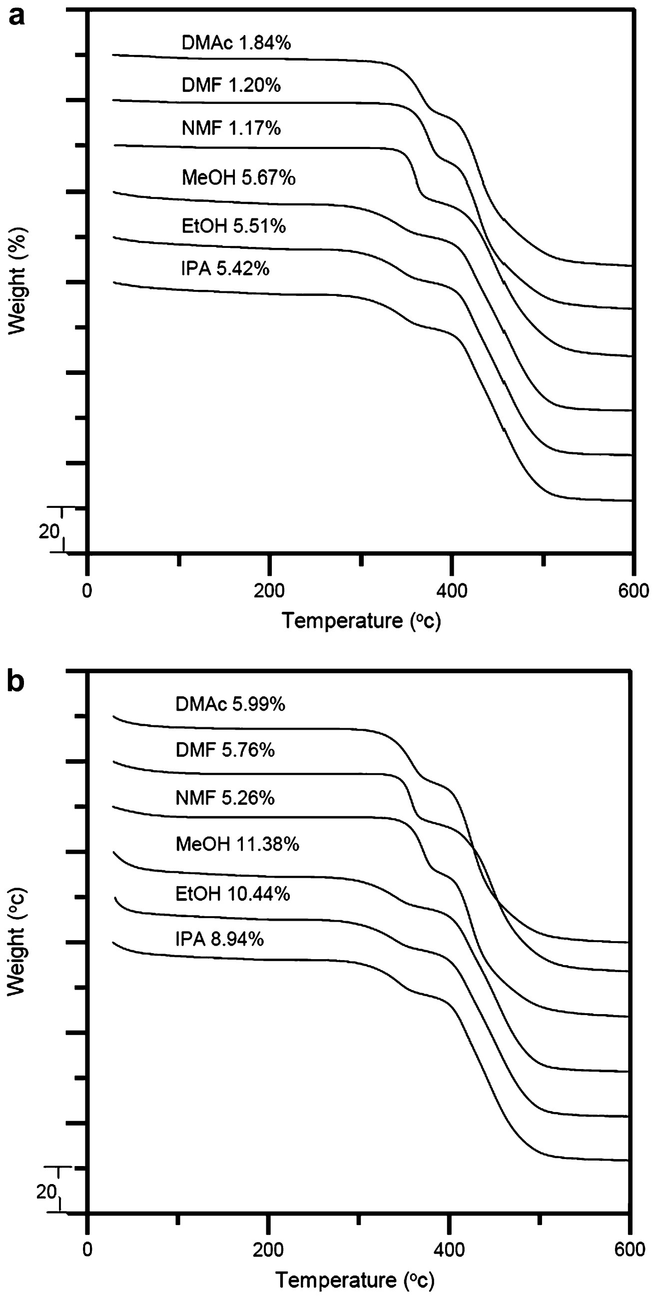


Fig. 4. (a) TGA data of Nafion membranes prepared by solution casting from various solvents and annealed at 150 °C for 90 min. The membranes were stored at 25 °C with 37% RH before TGA observations. (b) TGA data of Nafion membranes prepared by solution casting from various solvents and annealed at 150 °C for 90 min. The membranes were stored at 25 °C in distilled water before TGA observations.

The solution casting membranes were also annealed at 125 °C for 90 min and stored at 25 °C in distilled water. Their TGA scanning curves and data obtained from scanning curves are shown in Fig. 5 and Table 3, respectively. The TGA scanning curve and TGA data for commercial Nafion-117 membrane are also shown in Fig. 5 and

Table 2a
TGA data obtained from Fig. 4, membranes annealed at 150 °C and stored at 25 °C with 37% RH.

Solvent for preparing membranes	Water content (wt loss at temp < 250 °C)		1st decomposition temperature (°C)
	wt%	vol%	
DMAc	1.84	3.79	299.2
DMF	1.20	2.49	325.8
NMF	1.17	2.43	323.6
MeOH–H_2O (4/1 g/g)	5.67	11.2	274.5
EtOH–H_2O (4/1 g/g)	5.51	10.9	278.4
IPA–H_2O (4/1 g/g)	5.42	10.7	288.6

Table 3, respectively. Comparing Table 3 with Table 2b, we found the membranes annealed at 125 °C had similar casting solvent dependency of water uptake to the membranes annealed at 150 °C. From Tables 2b and 3, we also found that membranes annealed at 125 °C had higher water uptake than those annealed at 150 °C. It is known that the morphology of a Nafion membrane consists of hydrophilic ionic aggregation regions, hydrophobic perfluorocarbon backbone random-order aggregate amorphous regions, and hydrophobic perfluorocarbon backbone local order aggregate crystalline regions [23,27,31,47]. Annealing the membrane at a temperature above T_G induces local molecular motions and results in local order packing of perfluorocarbon backbones and thus the formation of crystalline regions. Raising annealing temperature from 125 °C to 150 °C increases the formation of local order crystalline regions. The crystalline sites act as physical crosslinks and retard water swelling in the membranes when the membranes are stored in distilled water [8,9]. Thus the water content of Nafion membranes decreased with increasing annealing temperature. Tables 2b and 3 also showed the commercial Nafion-117 membrane had higher water content than all the solution casting membranes when the membranes were annealed at 150 °C. However, Nafion-117 membrane had lower water content than membranes prepared by casting from alcohol–water mixture solutions and higher water content than the membranes prepared by casting from DMAc, DMF, and NMF solutions when the membranes were annealed at 125 °C.

3.4. DSC study

The influence of casting solvents on the degree of backbone aggregations and ether sulfonic acid group aggregations of Nafion membranes after annealing at 150 °C for 90 min was investigated using *DSC*. Figs. 6 and 7 show DSC data of membranes stored at 25 °C in a vessel with a humidity of 37% RH and in distilled water, respectively, after they were annealed at 150 °C for 90 min. Tables 4 and 5 summarize the data of peak temperatures and enthalpy of each endothermic peak of Figs. 6 and 7, respectively. The *DSC* low temperature endothermic enthalpy from 30 to 120 °C can be attributed to the evaporation of free water. The middle temperature endothermic enthalpy around 120–220 °C can be attributed to the evaporation of water associated with sulfonic acid groups. The endothermic enthalpy around 200–260 °C can be attributed to the dissociation of Nafion perfluorocarbon backbone aggregations [48–50]. However it is hard to separate three endothermic regions from DSC data, due to the overlap of these endothermic regions. In Figs. 6 and 7, DSC data showed two endothermic peaks and were separated into two peaks using Origin 6.0 software (Microcal Software Inc). In Tables 4 and 5, we show the data of endothermic peak temperature-1 and enthalpy-1 (T_1 and ΔH_1), endothermic peak temperature-2 and enthalpy-2 (T_2 and ΔH_2), and total enthalpy ($\Delta H_{total} = \Delta H_1 + \Delta H_2$). Enthalpy-1 is the combination of enthalpy contributed from the evaporation of free water and the evaporation of water associated with sulfonic acid groups. Enthalpy-2 is the combinations of enthalpy contributed from the evaporation of water associated with sulfonic acid groups and the dissociation of backbone aggregations. The results of Tables 4 and 5 show the membranes prepared from alcohol–water solvents have higher ΔH_1 and ΔH_2 values than those prepared from DMAc, DMF, and NMF, indicating the membranes prepared from alcohol–water solvents had higher water uptake and higher degree of perfluorocarbon backbone aggregations than those prepared from DMAc, DMF, and NMF solvents. The data of Tables 4 and 5 also show ΔH_1 and ΔH_2 data decrease when the solvents for preparing membranes varied from MeOH–H_2O to EtOH–H_2O and to IPA–H_2O. The DSC results are consistent with water uptake data obtained from TGA measurements as shown in Section 3.3.

Table 2b
TGA data obtained from Fig. 5, membranes annealed at 150 °C and stored at 25 °C in distilled water.

Solvents for preparing membranes	Water content (wt loss at temp < 250 °C)		1st decomposition temperature (°C)
	wt%	vol%	
DMAc	5.99	11.8	295.6
DMF	5.76	11.4	316.5
NMF	5.26	10.4	320.2
MeOH–H_2O (4/1 g/g)	11.38	21.2	269.3
EtOH–H_2O (4/1 g/g)	10.44	19.7	270.1
IPA–H_2O (4/1 g/g)	8.94	17.1	273.9

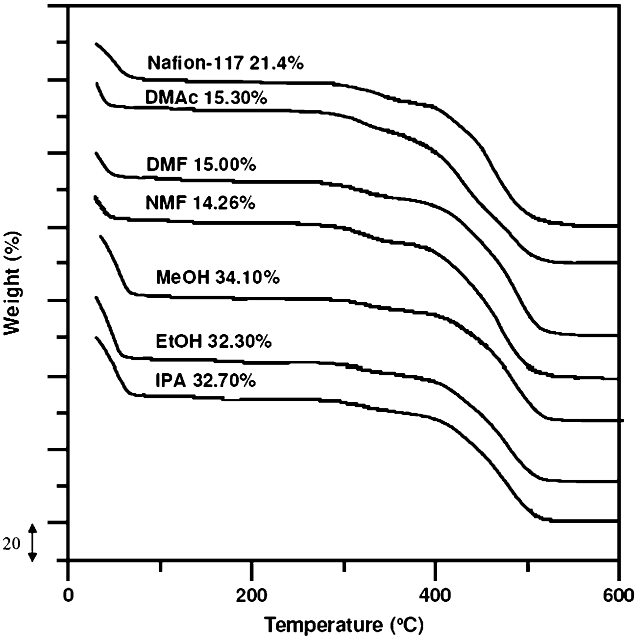


Fig. 5. TGA data of Nafion membranes prepared by solution casting from various solvents and annealed at 125 °C for 90 min. The membranes were stored at 25 °C in distilled water before TGA observations.

3.5. SAXS study

SAXS involves measurement of the scattering intensity as a function of the angle measured with respect to the direction of the incident X-ray beam. The scattering intensity arises due to local heterogeneities in the electron density of the material. For Nafion membranes, the heterogeneities come from the phase separation of

Table 3
TGA data obtained from Fig. 5, membranes annealed at 125 °C and stored at 25 °C in distilled water and Nafion-117 membrane.

Solvents for preparing membranes	Water content (wt loss at temp < 250 °C)		1st decomposition temperature (°C)
	wt%	vol%	
DMAc	15.30	27.5	274.5
DMF	15.00	27.0	274.1
NMF	14.26	25.9	272.7
MeOH–H_2O (4/1 g/g)	34.10	52.1	269.1
EtOH–H_2O (4/1 g/g)	32.32	50.1	267.6
IPA–H_2O (4/1 g/g)	32.71	50.5	267.8
Nafion-117	21.42	36.4	275.2

perfluorocarbon backbone aggregation crystalline structures, perfluorocarbon backbone amorphous domain, and ionic sulfonic acid group aggregations. For a phase-separation system, the invariant quantity Q of overall mean square electron density fluctuation is obtained by integrating $I(q)q^2$ all over the scattering angles.

$$Q = (1/2\pi)\int I(q)q^2\,dq \quad (5)$$

with

$$q = (4\pi/\lambda)\sin(\theta/2) \quad (6)$$

where q is the scattering vector, θ the scattering angle, λ the wavelength, $I(q)$ the scattering intensity at the scattering vector q.

Two basic features of Nafion membranes have been reported from small-angle scattering [22–31]: (1) a scattering maximum occurring at $q_{max} \sim 0.2$ Å^{-1} associating with aggregations of ionic sulfonic acid groups and (2) a scattering maximum occurring at $q_{max} \sim 0.07$ Å^{-1} associating with backbone aggregation crystalline features of the structure.

SAXS experiments were performed at 25 °C for Nafion membranes prepared by solution casting from various solvents and annealed at 150 °C for 90 min. Figs. 8 and 9 show the SAXS data of Nafion membranes stored at 25 °C with 37% RH and stored at 25 °C in distilled water, respectively. The average inter-domain distance, L, can be estimated from the q_m corresponding to the maximum of $I(q)q^2$ versus q curve using Bragg's equation:

$$L = 2\pi/q_m \quad (7)$$

Tables 6 and 7 show the inter-domain distance of perfluorocarbon backbone aggregation (L_{back}) and inter-domain distance of sulfonic acid ionic group aggregations (L_{ion}) of Nafion membranes stored at 25 °C with 37% RH and stored at 25 °C in distilled water, respectively.

Assuming the ionic sulfonic acid group aggregation regions are spheres and all the water molecules swollen in the membrane locate in the hydrophilic ionic aggregation regions, the radii R of ionic sulfonic acid group aggregations in wet membranes swollen with water and in dried membranes without water can be calculated from Eqs. (8a) and (8b), respectively [27]. The number N of $-SO_3H$ groups associated to each ionic sulfonic acid group aggregation can be calculated from Eqs. (9a) and (9b) for membranes swollen with water and for membranes without water, respectively [27]:

$$R = \{3/4\pi[\phi_w + v_{so3}(1-\phi_w)/v_0 - v_{so3}]\}^{1/3}L_{ion} \quad (\text{for } \phi_w > 0) \quad (8a)$$

$$N = L_{ion}^3(1-\phi_w)/(v_0 - v_{so3}) \quad (\text{for } \phi_w > 0) \quad (9a)$$

and

$$R = \{3/4\pi v_{so3}/v_0\}^{1/3}L_{ion} \quad (\text{for } \phi_w = 0) \quad (8b)$$

$$N = L_{ion}^3/v_0 \quad (\text{for } \phi_w = 0) \quad (9b)$$

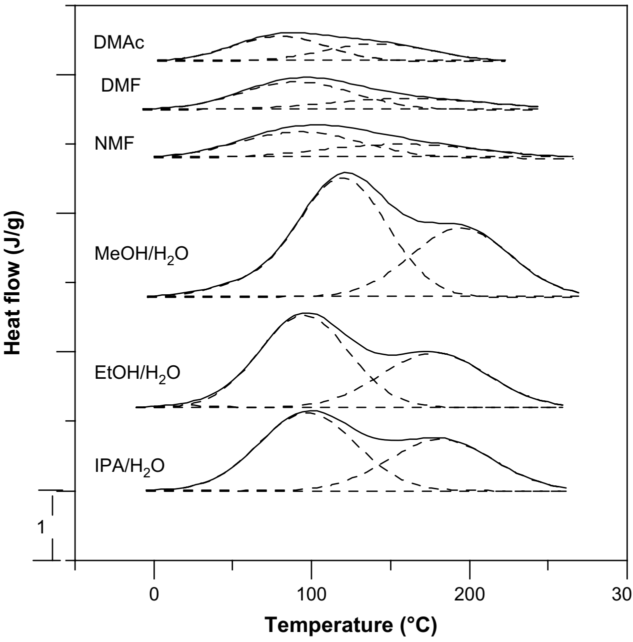


Fig. 6. DSC data of Nafion membranes prepared by solution casting from various solvents and annealed at 150 °C for 90 min. The membranes were stored at 25 °C with 37% RH before DSC observations. Full lines are experimental data and dashed lines are curve fitting data.

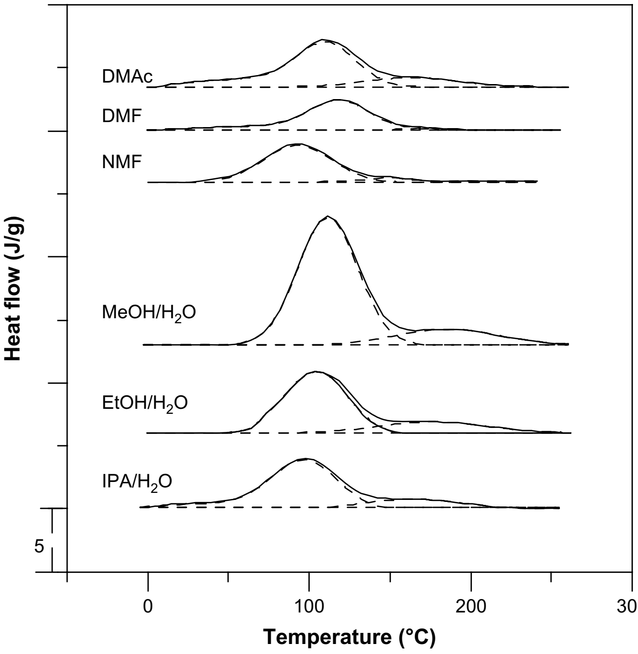


Fig. 7. DSC data of Nafion membranes prepared by solution casting from various solvents and annealed at 150 °C for 90 min. The membranes were stored at 25 °C in distilled water before DSC observations. Full lines are experimental data and dashed lines are curve fitting data.

Table 4
DSC data obtained from Fig. 6, membranes stored at 25 °C with 37% RH.

Solvents for membrane preparation	Peak-1		Peak-2		ΔH_{total} (J/g)
	T_1 (°C)	ΔH_1 (J/g)	T_2 (°C)	ΔH_2 (J/g)	
DMAc	81	31.9	140	23.8	55.6
DMF	91	32.2	163	18.2	50.4
NMF	95	25.8	158	18.0	43.8
MeOH–H_2O (4/1 g/g)	121	115.7	204	69.4	185.2
EtOH–H_2O (4/1 g/g)	94	96.6	176	66.4	163.1
IPA–H_2O (4/1 g/g)	99	92.6	180	65.8	158.4

where ϕ_w is the volume fraction of the swollen water, v_0 the average volume of dry polymer associated to one ionic –SO_3H group calculated from the equivalent weight ($v_0 = 870$ A^3 for dry Nafion), and v_{so3} the volume of one ionic –SO_3H group ($v_{so3} = 68$ A^3) [27]. The "*R*" and "*N*" values calculated from Eqs. (8a) and (9a), respectively, for annealed Nafion membranes stored at 25 °C with 37% RH and stored at 25 °C in distilled water are summarized in Tables 6 and 7, respectively.

The "*N*" value calculated from Eqs. (9a) and (9b) is equal to the value of the total number of ionic –SO_3H groups divided by the number of sulfonic acid group aggregation spheres in a membrane. The calculations of Eqs. (9a) and (9b) are based on the assumption that all the –SO_3H groups are located in the ionic aggregation regions. However, some of the ionic –SO_3H groups may locate in the amorphous regions and not in the ionic sulfonic acid group aggregations in the membranes. Assume the ionic –SO_3H groups in sulfonic acid group aggregated spheres distribute on the surfaces of spheres and without considering the electrostatic charge repulsion and excluded volume effect of the –SO_3H groups, the maximum number "*n*" of –SO_3H groups located in an ionic aggregated sphere can be calculated from Eq. (10).

$$n \sim R^2/(3v_{so3}/4\pi)^{2/3} \tag{10}$$

In Eq. (10), *n* is equal to the surface area of an ionic sulfonic acid group aggregated sphere divided by the surface area of a –SO_3H. The true number of –SO_3H groups located in an ionic –SO_3H aggregation spheres should be less than the *n* value calculated from Eq. (10), because of electrostatic charge repulsion and excluded volume effects among the –SO_3H groups. In Tables 6 and 7, we also summarize the *n* vales calculated from Eq. (10) and the *n*/*N* values, i.e. the ratio of possible maximum number of –SO_3H groups locate in an ionic sulfonic acid group aggregation sphere to the total –SO_3H groups associated to a sulfonic acid group aggregation in a membrane. These results revealed that not all the ionic –SO_3H groups were located in ionic –SO_3H aggregations. Comparing Tables 6 and 7 of SAXS data with Tables 2a and 2b of TGA data, we found approximately (though not exactly) the membranes with higher water content had higher *n*/*N* values. It is obvious increasing the volume fraction of water in Nafion membranes increases the possibility for vinylether –SO_3H groups to aggregate in the water rich ionic sulfonic acid group aggregation regions. And, thus the sizes of ionic –SO_3H group aggregations and the number of ionic –SO_3H groups located in ionic –SO_3H aggregation spheres increase with increasing water content of membranes. From the SAXS data shown in Tables 6 and 7, we found that Nafion membranes prepared from alcohol–water solutions had larger ionic

Table 5
DSC data obtained from Fig. 7, membranes stored at 25 °C in distilled water.

Solvents for membrane preparation	Peak-1		Peak-2		ΔH_{total} (J/g)
	T_1 (°C)	ΔH_1 (J/g)	T_2 (°C)	ΔH_2 (J/g)	
DMAc	113	162.9	162	29.1	196.0
DMF	120	171.6	173	11.0	182.6
NMF	91	172.6	150	8.6	181.1
MeOH–H_2O (4/1 g/g)	111	367.8	186	72.4	440.0
EtOH–H_2O (4/1 g/g)	104	311.4	178	70.8	382.1
IPA–H_2O (4/1 g/g)	98	228.3	167	66.9	295.2

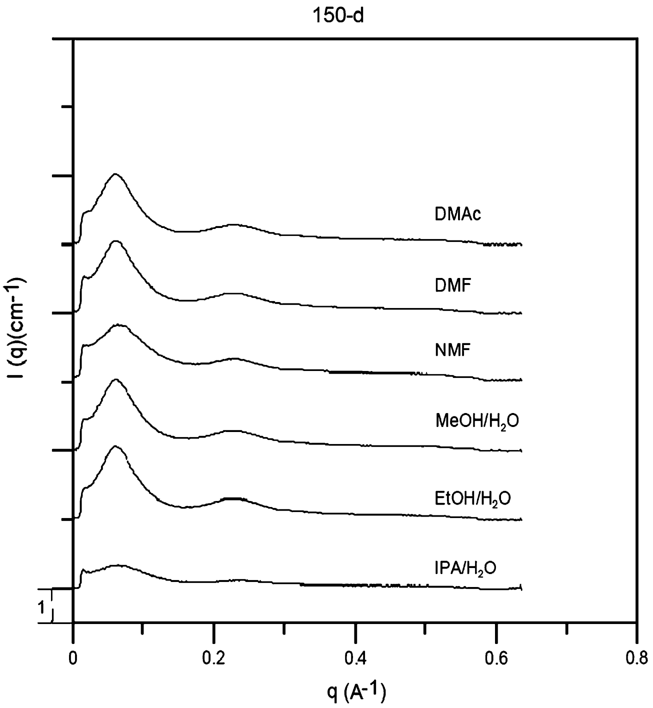


Fig. 8. SAXS data of Nafion membranes prepared by solution casting from various solvents and annealed at 150 °C for 90 min. The membranes were stored at 25 °C with 37% RH before SAXS study.

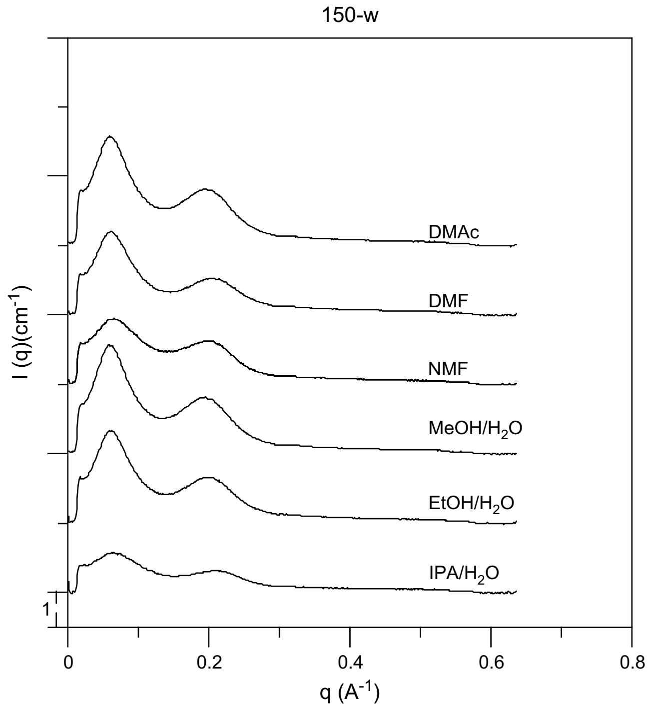


Fig. 9. SAXS data of Nafion membranes prepared by solution casting from various solvents and annealed at 150 °C for 90 min. The membranes were stored at 25 °C in distilled water before SAXS study.

Table 6
SAXS data obtained from Fig. 8, membranes stored at 25 °C with 37% RH.

Solvent	L_{back} (Å)	L_{ion} (Å)	N	R (Å)	n	n/N
DMAc	69.4	25.4	19.7	7.8	9.4	0.48
DMF	69.4	25.4	19.9	7.5	8.8	0.44
NMF	61.6	25.4	19.9	7.5	8.8	0.44
MeOH–H_2O (4/1 g/g)	68.8	25.6	18.6	9.1	12.9	0.70
EtOH–H_2O (4/1 g/g)	68.8	25.8	19.1	9.1	13.0	0.68
IPA–H_2O (4/1 g/g)	60.3	24.9	17.2	8.8	12.0	0.70

aggregation radii R and high n/N ratios than those prepared from DMAc, DMF, and NMF solvents. Though the data of Table 6 show no significant differences of R and n/N values in membranes prepared from alcohol–water mixture solvents, however, Table 7 shows that ionic aggregation sphere radius R and n/N ratio decrease when the solvent for preparing Nafion membranes varies from MeOH–H_2O to EtOH–H_2O and to IPA–H_2O. The data of Table 7 are consistent with the TGA data of water content of membranes.

3.6. Proton conductivity measurements

Nafion is one of the most important proton exchange membranes of PEMFC and DMFC (direct methanol fuel cell). Thus it should be interesting to compare the proton conductivity and methanol permeability of Nafion membranes prepared by solution casting with those of commercial Nafion-117 membrane. The membranes prepared by casting from various solvents and annealed at 150 °C and 125 °C under vacuum, then stored at 25 °C in distilled water were used for proton conductivity and methanol permeability measurements. There might be some residual solvents remained in the membranes when the membranes were prepared from high boiling temperature solvents (i.e. DMAc and NMF) and annealed at 125 °C. We changed water every day during membrane storage in distilled water. In this way, the influence of residual solvents on the properties of membranes was minimized.

Before conductivity measurements, the membranes were immersed in 0.5 M H_2SO_4 aqueous solution at 85 °C (85 °C < T_G of Nafion) for 1 h and then immersed in distilled water at room temperature for 10 min to clean the residual sulfuric acid on the surfaces of membranes. Tables 8a and 8b summarize the resistance r and conductivity σ data obtained at 70 °C with 95% RH for Nafion solution casting membranes annealed at 150 °C and 125 °C, respectively. The r and σ data of commercial Nafion-117 membrane are also shown in Table 8b for references. Each r datum was the average of three measurements with an error within 5%. The data show that the conductivity of a Nafion solution casting membrane is strongly influenced by the solvent used for membrane preparation. These data also show the conductivity of membranes prepared from alcohol–H_2O mixture solvents is much higher than that prepared from DMAc, DMF, and NMF solvents. The conductivity of a Nafion solution casting membrane decreases with casting solvent in the sequence of: MeOH–H_2O > EtOH–H_2O > IPA–H_2O > DMAc > DMF > NMF. Usually a membrane with a higher water content has a higher proton conductivity. The results of conductivity measurements are quite consistent, though not precisely, with the water uptake data of TGA, ΔH_{total} data of DSC, and n/N data of SAXS studies. The water uptake (Tables 2b and 3), ΔH_{total} (Table 5), and n/N (Table 7) values were higher for membrane prepared from alcohol–H_2O mixture solvents than from DMAc, DMF, and NMF solvents. Comparing Table 8a with Table 8b, we also found solution casting membranes annealed at 125 °C had higher proton conductivity than those annealed at 150 °C when the membranes were prepared from a same solvent. These results are also consistent with TGA data shown in Tables 2b and 3, which show the solution casting membrane annealed at 125 °C has a higher water content than that annealed at 150 °C when the membranes are prepared from a same solvent.

Table 7
SAXS data obtained from Fig. 9, membranes stored at 25 °C in distilled water.

Solvent	L_{back} (Å)	L_{ion} (Å)	N	R (Å)	n	n/N
DMAc	70.3	29.8	29.1	10.7	17.9	0.61
DMF	69.4	29.3	27.8	10.4	17.0	0.61
NMF	67.5	29.4	28.4	10.3	16.6	0.59
MeOH–H_2O (4/1 g/g)	71.4	29.5	25.2	12.0	22.4	0.89
EtOH–H_2O (4/1 g/g)	71.4	29.4	25.5	11.7	21.5	0.84
IPA–H_2O (4/1 g/g)	66.3	28.6	24.2	11.1	19.2	0.79

Table 8a
Membrane thickness d, resistance r and conductivities σ at 70 °C and 95% RH for Nafion solution casting membranes annealed at 150 °C and stored at 25 °C in distilled water.

Solvent	d (10^{-2} cm)	r (Ω)	σ (10^{-3} S/cm)
DMAc	1.72	1.26	4.34
DMF	1.73	3.04	1.81
NMF	1.71	3.99	1.36
MeOH–H_2O	1.74	0.315	17.6
EtOH–H_2O	1.75	0.687	8.11
IPA–H_2O	1.74	0.791	7.01

Du Pont Nafion-117 membrane is one of the most successful PEMs used in DMFC. It is known that Nafion-117 membrane was manufactured by extrusion. But we don't know the annealing temperature for preparing Nafion-117. In order to compare the proton conductivity of Nafion solution casting membranes with that of Nafion-117 membrane, the r of Nafion-117 was also measured at 70 °C with 95% RH and the r and σ data are listed in Table 8b. Investigating the σ values listed in Tables 8a and 8b, we found σ value of Nafion-117 was slightly lower than that of alcohol–H_2O mixture solution casting membranes annealed at 125 °C but higher than that of alcohol–H_2O mixture solution casting membranes annealed at 150 °C. However, the σ value of Nafion-117 was much higher than that of DMAc, DMF, and NMF solution casting membranes annealed both at 125 °C and 150 °C.

3.7. Methanol permeability measurements

The membranes annealed at 150 °C and 125 °C under vacuum and then stored at 25 °C in distilled water were used for methanol permeability measurements. The methanol crossover measurements of membranes were carried out at 30 °C and 70 °C for 10 h. Fig. 10a and b shows the plots of $C_b(t)$ versus t of Eq. (2) for methanol crossover measurements at 30 °C and 70 °C, respectively, for Nafion solution casting membranes annealed at 150 °C. Fig. 11a and b shows the plots of $C_b(t)$ versus t of Eq. (2) for methanol

Table 8b
Membrane thickness d, resistance r and conductivities σ at 70 °C and 95% RH for Nafion solution casting membranes annealed at 125 °C and stored at 25 °C in distilled water.

Solvent	d (10^{-2} cm)	r (Ω)	σ (10^{-3} S/cm)
DMAc	1.77	0.247	22.8
DMF	1.75	0.547	9.72
NMF	1.78	0.648	8.81
MeOH–H_2O	1.77	0.097	58.1
EtOH–H_2O	1.76	0.106	52.9
IPA–H_2O	1.74	0.116	47.6
Nafion-117	1.76	0.128	43.8

crossover measurements at 30 °C and 70 °C, respectively, for Nafion-117 membrane and Nafion solution casting membranes annealed at 125 °C. The $C_b(t)$ datum was the average of three measurements with an error within 5%. The methanol permeability P datum of each membrane was obtained from the slope of $C_b(t)$ versus t plot. Tables 9 and 10 summarize the P data obtained at 30 °C and 70 °C for Nafion solution casting membranes annealed at 150 °C and 125 °C, respectively. The P data of Nafion-117 membrane obtained at 30 °C and 70 °C are also listed in Table 10. The behavior of casting solvent dependency of P data shown in Tables 9 and 10 was similar to the casting solvent dependency of σ data shown in Tables 8a and 8b. The membranes prepared from alcohol/water mixture solvents had much higher P values than those prepared from DMAc, DMF, and NMF solvents. From Tables 9 and 10, we found P value decreased with the solvent used for membrane preparation in the sequence of: MeOH–H_2O > EtOH–H_2O > IPA–H_2O > DMAc > DMF > NMF. These results were also consistent with the water content data of TGA, ΔH_{total} (∼enthalpy of water evaporation) data of DSC, and n/N values of SAXS studies. It is obvious that Nafion membranes consisting of larger ionic aggregations have higher water content after swollen with water. Because of high compatibility of methanol with water, the membranes containing more water should be more feasible for methanol permeation.

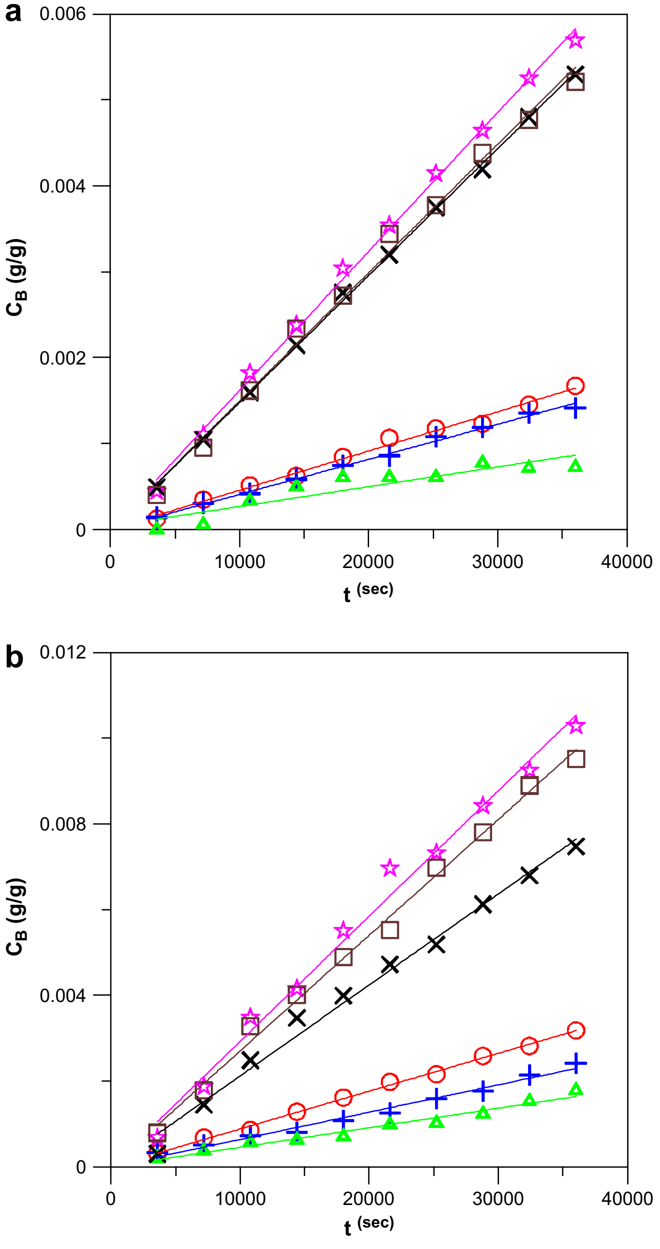


Fig. 10. (a) Plots of $C_b(t)$ versus t of Eq. (2) for methanol crossover measurements at 30 °C of Nafion membranes prepared from various solvents and annealed at 150 °C for 90 min. Solvents for membrane preparations: (○) DMAc; (+) DMF; (△) NMF; (☆) MeOH–H_2O; (□) EtOH–H_2O; (×) IPA–H_2O. (b) Plots of $C_b(t)$ versus t of Eq. (2) for methanol crossover measurements at 70 °C of Nafion membranes prepared from various solvents and annealed at 150 °C for 90 min. Solvents for membrane preparations: (○) DMAc; (+) DMF; (△) NMF; (☆) MeOH–H_2O; (□) EtOH–H_2O; (×) IPA–H_2O.

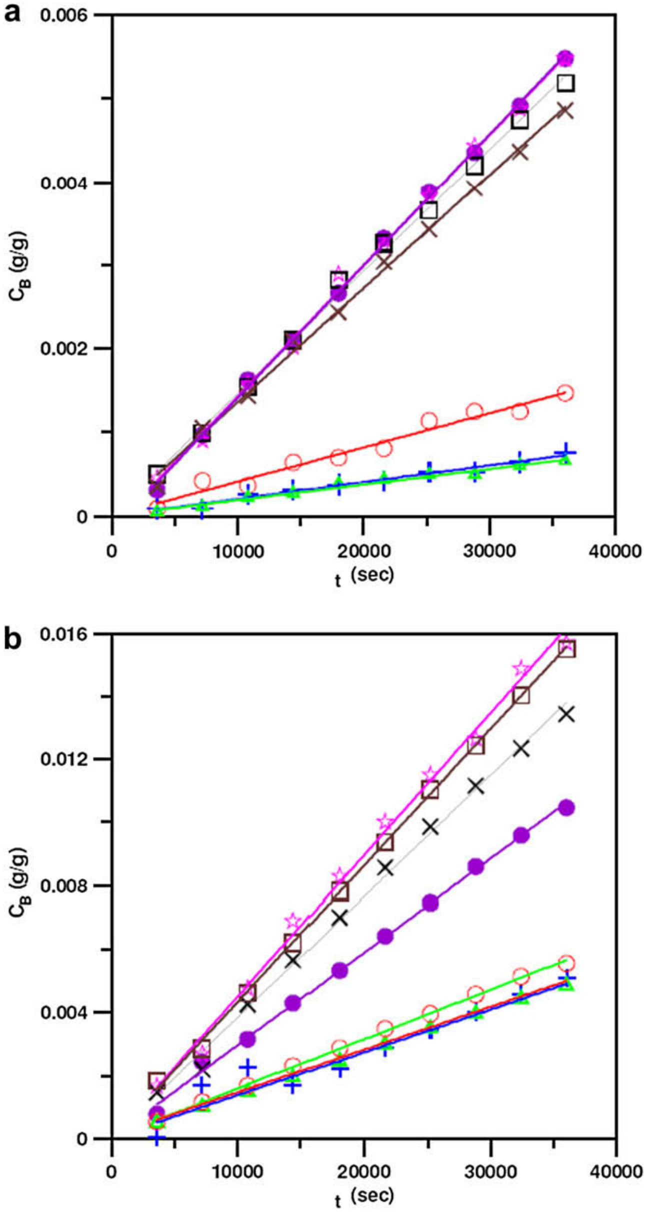


Fig. 11. (a) Plots of $C_b(t)$ versus t of Eq. (2) for methanol crossover measurements at 30 °C of Nafion membranes prepared from various solvents and annealed at 125 °C for 90 min. Solvents for membrane preparations: (○) DMAc; (+) DMF; (△) NMF; (☆) MeOH–H_2O; (□) EtOH–H_2O; (×) IPA–H_2O; (•) Nafion-117. (b) Plots of $C_b(t)$ versus t of Eq. (2) for methanol crossover measurements at 70 °C of Nafion membranes prepared from various solvents and annealed at 125 °C for 90 min. Solvents for membrane preparations: (○) DMAc; (+) DMF; (△) NMF; (☆) MeOH–H_2O; (□) EtOH–H_2O; (×) IPA–H_2O; (•) Nafion-117.

Table 9
Methanol permeability P at 30 °C and 70 °C of Nafion membranes prepared from various solvents and annealed at 150 °C for 90 min. (The value in bracket is the error of linear curve fitting shown in Fig. 10a and b).

Solvent	P (10^{-6} cm^2/s) at 30 °C	P (10^{-6} cm^2/s) at 70 °C
DMAc	0.505 (±2.0%)	1.60 (±1.2%)
DMF	0.430 (±1.5%)	1.20 (±2.7%)
NMF	0.228 (±6.2%)	0.923 (±3.6%)
MeOH/H_2O	2.32 (±1.1%)	4.44 (±2.0%)
EtOH/H_2O	2.24 (±1.0%)	4.11 (±1.5%)
IPA/H_2O	2.21 (±1.7%)	3.40 (±2.2%)

Carefully investigating the P data shown in Tables 9 and 10, we found the annealing temperature of a solution casting membrane had great influence on the P value measured at 70 °C. The membranes annealed at 125 °C had higher P values at 70 °C than those annealed at 150 °C when the membranes were prepared from a same casting solvent. Raising the annealing temperature of a membrane increases the formation of perfluorocarbon backbone crystalline. The crystalline sites reduce the mobility of Nafion molecules and retard the methanol permeability in membranes at 70 °C which is around 30 °C below T_G of solid Nafion resin. However, Tables 9 and 10 showed the annealing temperature had little influence on the P value at 30 °C for membranes prepared from a same casting solvent. The experimental results showed the membranes annealed at 125 °C had similar P values at 30 °C to those annealed at 150 °C when the membranes were prepared from a same casting solvent.

In order to compare the methanol permeability of Nafion solution casting membranes with that of Nafion-117 membrane (a benchmark PEM of DMFC), the plots of $C_b(t)$ versus t of methanol crossover measurements at 30 °C and 70 °C of Nafion-117 are also shown in Fig. 11a and b, respectively. The P values at 30 °C and 70 °C of Nafion-117 obtained from Fig. 11a and b, respectively, are also listed in Table 10. Carefully investigating the P values at 70 °C listed in Tables 9 and 10, we found that P value at 70 °C of Nafion-117 was close to that of alcohol–H_2O solution casting membranes annealed at 150 °C but lower than that of alcohol–H_2O solution casting membranes annealed at 125 °C. However, the P value at 70 °C of Nafion-117 was higher than that of DMAc, DMF, and NMF solution casting membranes annealed both at 125 °C and 150 °C. Investigating the P values at 30 °C listed in Tables 9 and 10, we found that P value at 30 °C of Nafion-117 was close to that of alcohol–H_2O solution casting membranes annealed both at 125 °C and 150 °C. The P value at 30 °C of Nafion-117 was also higher than that of DMAc, DMF, and NMF solution casting membranes annealed both at 125 °C and 150 °C.

In summary of σ (Table 8b) and P (Table 10) data of Nafion-117, we found the σ and P values of Nafion-117 were closer to those of Nafion membranes prepared by solution casting from alcohol–H_2O solutions rather than from DMAc, DMF, and NMF solutions. These results may suggest the morphology of Nafion-117 membrane is similar to the membranes prepared by casting from alcohol–H_2O solutions rather than from DMAc, DMF, and NMF solutions. In literature [23,27,31,50], it had been reported the morphology of Nafion-117 membranes consists of hydrophilic ionic aggregation regions and hydrophobic perfluorocarbon backbone aggregate amorphous and crystalline regions. The hydrophobic perfluorocarbon backbone aggregations of Nafion-117 are similar to the Nafion perfluorocarbon backbone aggregations of membranes prepared by solution cast from alcohol–H_2O solvents as shown in Fig. 3.

Table 10
Methanol permeability P at 30 °C and 70 °C for Nafion membranes prepared from various solvents and annealed at 125 °C for 90 min. (The value in bracket is the error of linear curve fitting shown in Fig. 11a and b).

Solvent	P (10^{-6} cm^2/s) at 30 °C	P (10^{-6} cm^2/s) at 70 °C
DMAc	0.649 (±3.7%)	2.18 (±1.0%)
DMF	0.461 (±3.0%)	2.06 (±5.4%)
NMF	0.288 (±3.5%)	1.94 (±1.0%)
MeOH/H_2O	2.45 (±1.1%)	6.54 (±1.5%)
EtOH/H_2O	2.33 (±1.1%)	6.37 (±1.0%)
IPA/H_2O	2.20 (±1.1%)	5.58 (±1.3%)
Nafion-117	2.25 (±0.5%)	4.36 (±1.0%)

4. Conclusions

Nafion molecular conformations in dilute solutions and the morphology of Nafion membranes prepared by solution casting from DMAc, DMF, NMF, MeOH–H_2O, EtOH–H_2O, IPA–H_2O solutions were investigated. The experimental results showed the Nafion molecular conformations in dilute solutions and the morphology of membranes prepared from solution castings were strongly influenced by δ and ε of solvents. The Nafion molecules behave coiled-like structures with low molecular aggregations in dilute DMAc and DMF solutions, in which the solvents have low ε and with δ closing to $\delta_1 = 9.7$ $(cal/cm^3)^{1/2}$ of Nafion perfluorocarbon backbone. The DSC ΔH data and SAXS R and n/N data showed low ionic –SO_3H aggregations in membranes when membranes were prepared from DMAc and DMF solutions. The Nafion molecules behave mixture of rod-like and rectangle-like structures with small molecular aggregations in NMF solution, in which the solvent has a high ε and a δ closing to $\delta_2 = 17.3$ $(cal/cm^3)^{1/2}$ of Nafion vinylether side chains. The DSC ΔH data and SAXS R and n/N data showed low degree of perfluorocarbon backbone aggregations and low ionic –SO_3H aggregations in membranes prepared from NMF solutions. Nafion molecules aggregate in dilute alcohol–water solutions, in which the solvents have low ε and with δ closing to $\delta_2 = 17.3$ $(cal/cm^3)^{1/2}$ of Nafion vinylether side chains. The DSC ΔH data and SAXS R and n/N data showed high degree of perfluorocarbon backbone aggregations and high ionic –SO_3H aggregations in membranes prepared from alcohol–water mixture solutions. The TGA, conductivity measurements, and methanol permeability measurements showed low water uptake, low proton conductivity, and low methanol permeability for membranes prepared from DMAc, DMF, and NMF solvents and high water uptake, high proton conductivity, and high methanol permeability for membranes prepared from alcohol–water solvents. For membranes prepared from alcohol–water solutions, the water uptake, proton conductivity, and methanol permeability of membranes decrease with solvents for membrane preparation in the sequence of: MeOH–H_2O < EtOH–H_2O < IPA–H_2O. These phenomena can be attributed to the decreases of perfluorocarbon backbones and sulfonic acid group aggregations when the solvent for membrane preparations is varied from MeOH–H_2O to EtOH–H_2O, and to IPA–H_2O, because the δ of solvent becomes closer to $\delta_1 = 9.7$ $(cal/cm^3)^{1/2}$ of Nafion perfluorocarbon backbone when the solvent is varied from MeOH–H_2O to EtOH–H_2O, and to IPA–H_2O. The proton conductivity and methanol permeability of commercial Nafion-117 membrane were also investigated and compared with those of Nafion solution casting membranes annealed at 125 °C. The experimental results revealed that Nafion-117 had properties similar to the solution casting membranes prepared from alcohol–H_2O solvents rather than from DMAc, DMF, and NMF solvents.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.01.060.

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