

FT-IR study of the microstructure of Nafion® membrane

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Abstract

Nafion® membrane is a key component of polymer electrolyte membrane fuel cell. In this paper, transmission and attenuated total reflection (ATR) spectra of Nafion® membrane and the difference of absorption peaks between two modes are presented. The peak shift is attributed to the different chemical environments of surface and bulk. Obvious change was observed after thermal treatment on Nafion® membrane through calculation of the relative absorption intensity ratio of different groups. It was found that side chain may move out of the bulk to the surface for the membrane. And the moving degree increased with the treating temperature.

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1. Introduction

Nafion® membrane (DuPont Corp.) has attracted more attention for its wide utilization in chlor-alkali technologies and proton exchange membrane fuel cells (PEMFCs). Numerous studies on its microstructure and properties have been carried out with various methods in the past 30 years [1]. This material has a perfluoroethylene backbone with side chains of perfluorinated vinyl-ethers terminated by sulfonic group.

For the microstructure, Hsu and Gierke [2] proposed the following model based on small angle X-ray scattering (SAXS) results: ionic clusters of 3–5 nm in diameter connected by channel of 1–1.5 nm are dispersed in the hydrophobic organic medium; the average cluster contains ca. 70 ion exchange sites and 1000 water molecules. Falk and co-workers [3,4] suggested that the hydrated ion clusters are smaller than that of Gierke's model and are not spherical, with local intrusion of the fluorocarbon phase. A three-phase mode, in which fluorocarbon crystallites, ionic hydrophilic clusters and an amorphous hydrophobic region of lower ionic water content coexist, has been proposed by Yeager and Steck [5] and Pineri et al. [6]. Imaging the tap-

ping mode of an atomic force microscope (AFM) has been used to identify the hydrophobic and hydrophilic regions of Nafion®. The images support the cluster model with a range of size from 5 to 30 nm, depending on the water content [7].

Infrared spectroscopy has been applied as a useful method to study Nafion® membranes [3,4,7–17]. Numerous studies were focused on the state of water in the membrane and the influences of different cations on sulfonate symmetric stretching mode.

The surface of Nafion® membrane, due to the ionomer microstructure, has been regarded as the coexistence of hydrophobic and hydrophilic regions. To avoid 'zero gap' effect [18] and to magnify the three-phase boundary, it is necessary to improve the hydrophilic properties of the surface. But the modification methods that have been applied so far cannot meet the requirement of membrane electrode assembly (MEA) fabrication for PEMFC. Structural modification of membrane surface is an ideal method through special treatment. Kanamura [19] figured that the SO₃⁻ group might slightly move out from the Nafion bulk to the interface region, which is induced by the injection of 0.1 mol dm⁻³ HClO₄ aqueous solution.

In this paper, we compare the infrared spectra of Nafion membrane at transmission mode and attenuated total reflection (ATR) mode. The difference was explained with the different structure between surface and bulk. Additional study of Nafion membrane fabricated at lower temperature

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remains micelle structure, which differs from commercial membrane.

2. Experimental section

2.1. Materials

Nafion[®] 115 membrane purchased from DuPont Corp. was pretreated by means of conventional process, boiling it in 3% H₂O₂, in deionized water, in 0.5 M H₂SO₄, and in deionized water for at least 1 h for each step, respectively.

To prepare the in-house Nafion membrane, 5% commercial Nafion solution with addition of some high boiling solvent was cast onto a glass plate, evaporated at 60 °C, and peeled off in deionized water. The obtained membrane was also pretreated in the way described previously.

To obtain thin Nafion membrane of ca. 1 μm, a drop of 5% commercial Nafion solution with addition of some high boiling solvent was spread on AgCl film, evaporated at 60 °C and then dried at 130 °C for 0.5 h.

Nafion[®] 115 membrane was treated at different temperatures of –40, 120, 150 and 180 °C, respectively for 1.5 h in a vacuum oven. To avoid transmutation of the membrane, the membrane was placed in two glass plates, which was pressed between two PTFE films first. ATR spectrum was collected afterwards.

2.2. FT-IR spectroscopy

The spectra were collected on a Nicolet Avatar-370 equipped with a DTGS detector and a ZnSe crystal (45°

Table 1
Selected infrared absorption bands of H-Nafion

Band location (cm ⁻¹)	Assignment
~1200 vs ^a , vbr ^b	CF ₂ stretching, asymmetric
~1100 vs, vbr	CF ₂ stretching, symmetric
~1060 s	S–O stretching, symmetric
~980 s	C–F stretching (–CF ₂ –CF(CF ₃)-group)
~960 s	C–O–C stretching, symmetric

^a Relative intensity: vs, very strong; s, strong.

^b Band width: vbr, very broad.

angle) as attenuated total reflection accessory. A spectrum, collected as the average of 64 scans with a resolution of 4 cm⁻¹, was recorded from 4000 to 400 cm⁻¹ for the transmission mode, while from 4000 to 650 cm⁻¹ for the ATR. Nafion[®] 115 membrane was used and the pressure was equal in all ATR measurements to avoid the difference brought by the pressure and penetrating depth.

All spectra were collected with Omnic 6.1a. Calculation of the integrated area was conducted with the same software.

3. Results and discussion

3.1. Assignment of the IR absorption bands of IR spectra and analysis of peak situation

The assignment of the vibrational bands of Nafion was based on the already published data [3,4,7–17]. The main absorption bands and corresponding assignment are listed in Table 1.

Fig. 1 shows the transmission spectrum and the ATR spectrum. The main peaks are listed in Table 2. $\nu_{as}(\text{CF}_2)$

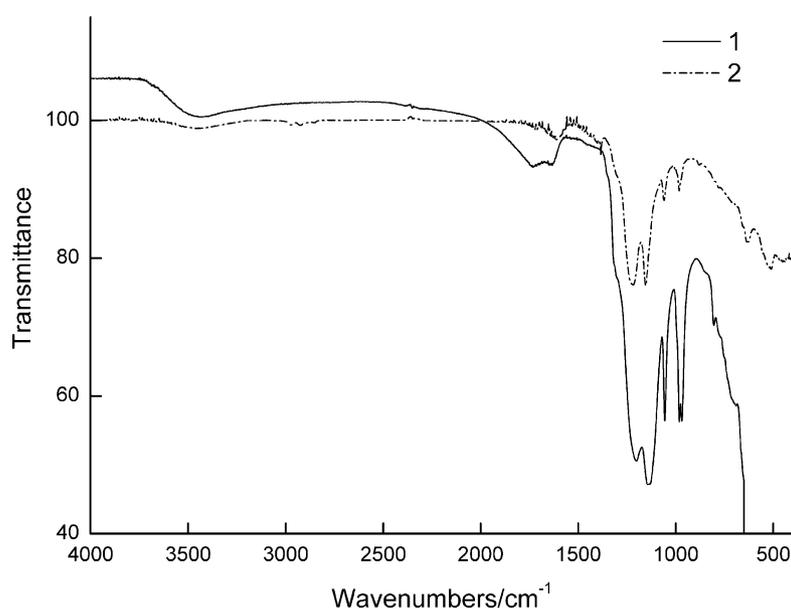


Fig. 1. Infrared spectra of Nafion membrane. (1) ATR spectrum of Nafion[®] 115 membrane. (2) Transmission spectrum of Nafion membrane on AgCl film (baseline correlated).

Table 2
Absorption peaks of different Nafion membranes

	$\nu_{as}(\text{CF}_2)$	$\nu_s(\text{CF}_2)$	$\nu_s(\text{SO})$	$\nu_s(\text{CFRCF}_3)$	$\nu_s(\text{COC})$
ATR of dried H-Nafion [®] 115 membrane	1201.5	1143.2	1056.0	981.4	968.9
Transmission spectrum of thin Nafion membrane on AgCl film	1221.1	1154.2	1060.5	982.4	Shoulder

Table 3
Comparison of different Nafion membranes^a

	1	2
$\nu_s(\text{SO})$ (cm^{-1})	1058.3	1070.6

^a The number is corresponding to IR spectrum in Fig. 2.

of ATR spectra is red-shifted by 20.4 cm^{-1} compared with that of transmission IR. The shift of $\nu_s(\text{CF}_2)$ and $\nu_s(\text{SO})$ is 10.7 and 4.8 cm^{-1} , respectively. ATR is a surface infrared technology, for which the penetration depth is about several micrometers, while transmission spectrum is the average information. The obvious red shift between the two spectra indicates that chemical environment is different for membrane surface and bulk. It is reasonable to conclude that the concentration of CF_2 group representing the main chain in the bulk is higher than in the surface. Gardner [20] reported that conductance in the tangential direction is three times higher than that in the normal direction, which is in agreement with the IR anisotropy only from the conductance data.

Fig. 2 shows the transmission spectra of different membranes. Comparison between the transmission spectra of thin Nafion membranes fabricated on AgCl film, $\nu_s(\text{SO})$ shifts to higher wavenumber after thermal treatment, which is listed in Table 3.

This blue shift may result from the reorganization of microstructure. Fabricated at low temperature, Nafion membrane remains the micelle structure and is soluble in hot water before thermal treatment. After thermal treatment, the main chain crystallizes and the microstructure turns 'inverted micelle'. Sulfonic group aggregates to clusters in crystalline region.

Additionally, the unobvious shift of $\nu(-\text{CFRCF}_3)$ is probably due to its situation between the main chain and $-\text{SO}_3\text{H}$ group.

3.2. Peak shape

The relative intensity of $\nu_{as}(\text{CF}_2)$ to $\nu_s(\text{CF}_2)$ is obviously different for the transmission spectrum and ATR spectrum. The causes need developing studies.

3.3. Influence of temperatures on Nafion[®] 115 membrane

Nafion[®] 115 membranes were treated at different temperatures for 1.5 h, with ATR spectrum collected afterwards. Calculation is conducted for the ATR spectra. The integrated area is calculated in the following region. All these regions are selected as the half of the peaks because of the overlap of

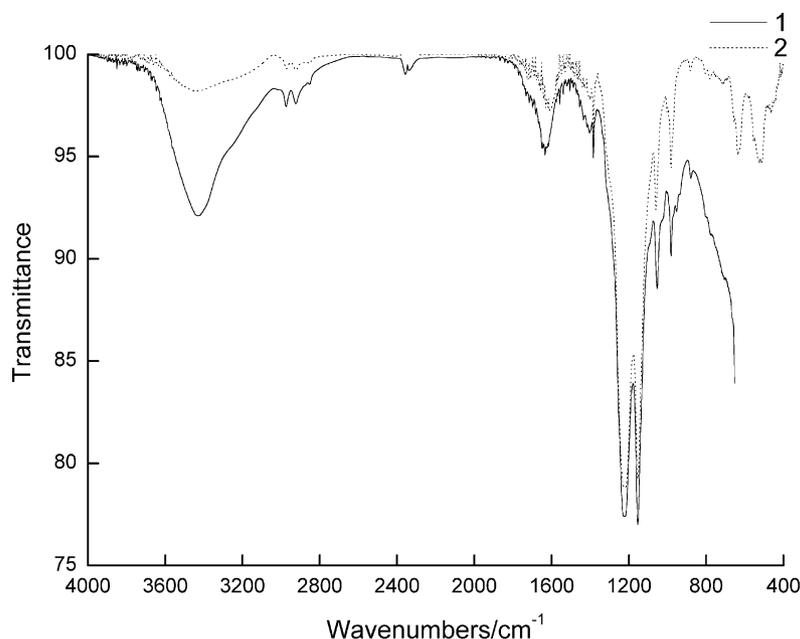


Fig. 2. Transmission spectra of different Nafion membranes. (1) Nafion membrane fabricated on AgCl film at $40\text{ }^\circ\text{C}$. (2) Nafion membrane fabricated on AgCl film after $130\text{ }^\circ\text{C}$ for 30 min.

Table 4
The integrated area of different peaks

	CF ₂	SO ₃ H	CFRCF ₃	COC
In-house Nafion membrane	6207.5	267.0	304.6	486.6
Nafion [®] 115 membrane treated at 40 °C for 1.5 h	4662.5	161.1	205.8	297.7
Nafion [®] 115 membrane treated at 120 °C for 1.5 h	4768.8	180.8	202.9	335.5
Nafion [®] 115 membrane treated at 150 °C for 1.5 h	5867.8	255.9	293.3	471.2
Nafion [®] 115 membrane treated at 180 °C for 1.5 h	5574.7	245.0	264.4	424.4

neighboring peaks. And the selected peaks are all relatively symmetrical and unsaturated:

- For CF₂ group, 1369.3–1203.4 cm⁻¹.
- For SO₃H group, 1056.8–1014.4 cm⁻¹.
- For CFRCF₃ group, 1010.6–981.6 cm⁻¹.
- For COC group, 968.1–887.1 cm⁻¹.

The results were listed in Table 4.

The relative area ratio of SO₃H to CF₂, COC to CF₂, CFRCF₃ to CF₂ are shown in Figs. 3–5. X-coordinate represents the treatment temperature. The point at 0 °C is corresponding to the in-house Nafion membrane fabricated at 60 °C. It is well known that side chain starts moving and some main chains may change in conformation at temperatures above *T_g*. The relative ratio of SO₃H to CF₂ and COC to CF₂ increases with the treatment temperature in the whole. The maximum ratio change is about 30% and the trend for SO₃H group and COC group is similar. So the change should not be regarded as experimental error. But after treatment at 180 °C, the color of the polymer turns dark brown. This phenomenon may be resulted from the decomposition of Nafion. The relative area ratio of CFRCF₃ to CF₂ could be regarded as constant (the ratio changes within 10%) during thermal treatment, which may be the result of

the similarity of CFRCF₃ group with the main chain. During the aggregation of side chains, CFRCF₃ group is embedded in the crystalline region.

It is likely that side chain moves from the bulk to the surface. Water loss causes the shrinkage of clusters in size, while the number increases. Because of the high surface energy, aggregation of clusters, brought by side chain movement, may occur to form larger ones during thermal treatment, while it will not happen in the bulk because crystalline of the main chain is the major factor for decreasing the whole energy of the system, which prevents the clusters from aggregating.

All the peaks shift to lower wavenumber, which indicates the changes of chemical surrounding. So as to the relatively high ratio of the in-house Nafion membrane, it is probably due to the micelle structure different from the inverted micelle structure of commercial Nafion[®] membrane.

The structure change may also affect coefficient of extinction of different functional groups. Thus the absorption change may also be affected by the coefficient change. However, there is one definite point that the surface and the bulk experienced obvious changes during thermal treatment.

Additionally, we observed an unpublished peak at 1017 cm⁻¹ previously, which change little during the

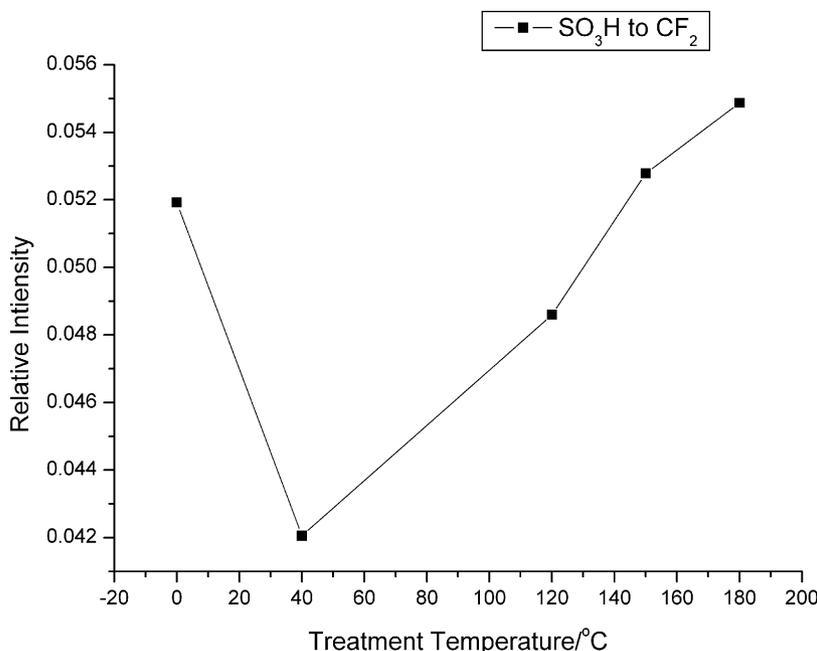
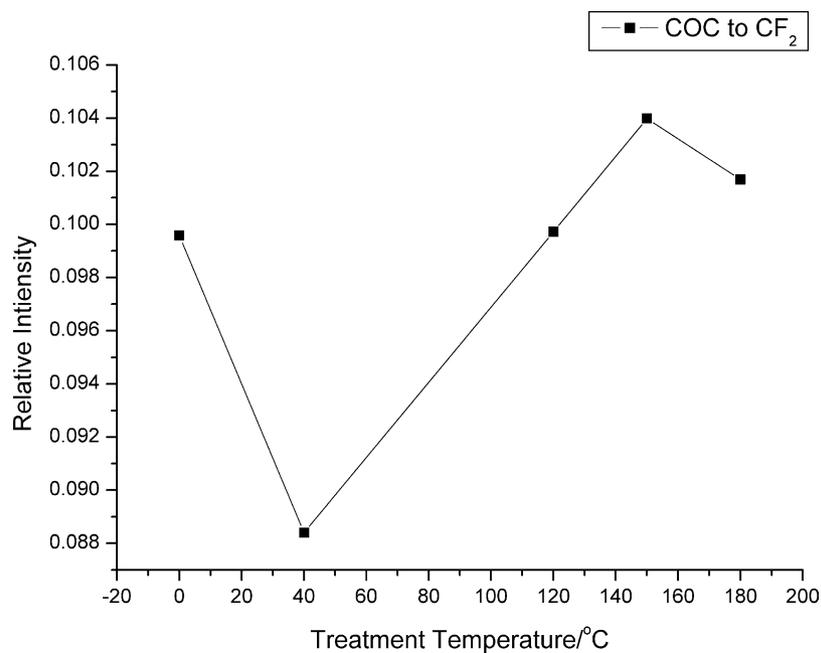
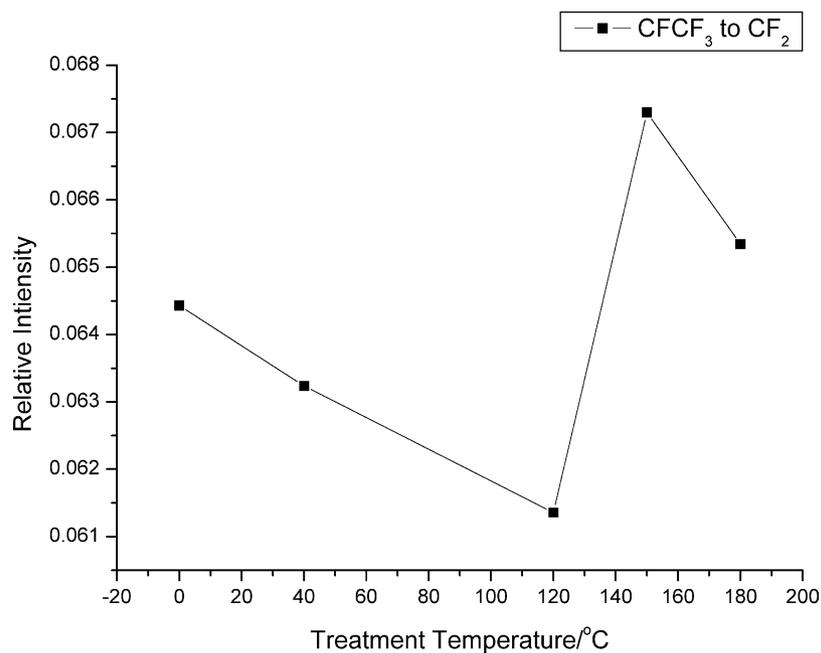


Fig. 3. The relative intensity of SO₃H to CF₂.

Fig. 4. The relative intensity of COC to CF₂.Fig. 5. The relative intensity of CF₃CF to CF₂.

process of water loss. We attribute it to the asymmetric stretching of C–O–C group.

4. Conclusion

FT-IR result evidences the microstructural differences between surface and bulk of Nafion[®] membrane. In membrane surface, the macromolecule remains micelle structure and –SO₃H is free from the surrounding of the main chain. Thermal treatment causes the membrane to change in structure

and physical properties. At temperatures above T_g , side chain movement brings the –SO₃H group out of the bulk to the surface to decrease the surface energy. The thermodynamics of membrane treatment needs more study in the future.

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