

Manuscript of  
Journal of Power Sources, 180, 733-737(2008)

## Slow Morphological Change of Perfluorinated Ionomer as Deduced From $^1\text{H}$ NMR Spectra of Confined Water

Atsuko Y. Nosaka, and Yoshio Nosaka\*

Department of Chemistry, Nagaoka University of Technology

Nagaoka, 940-2188, Japan

\* *Corresponding author.* Tel/fax: +81-258-47-9315

E-mail address: [nosaka@nagaokaut.ac.jp](mailto:nosaka@nagaokaut.ac.jp)

### Abstract

The behaviour of water molecules confined in the perfluorinated ionomer membrane, which is widely used for polymer electrolyte fuel cells, was investigated by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectra of water molecules confined in the membrane presented characteristic features depending on temperature and hydrated conditions. On the basis of the observations of the variations in the  $^1\text{H}$  NMR signals, it was deduced that the polymer underwent very slow conversions among distinct morphologies depending on temperatures and humidified conditions below 348 K. A plausible scheme of the local conversion of the states of the water molecules associated with the morphological changes of the polymer was proposed.

*Keywords:* Perfluorinated ionomer; Nafion; NMR; Water; Morphology

## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising as a device for clean and efficient energy conversion [1-3]. To prolong the lifetime is one of the most concerns for practical use of PEFCs. For this purpose, one of the most urgent technical problems that should be circumvented is to prevent the polymer electrolyte membrane employed for PEFCs from the deterioration during the operations. However, the detailed mechanism for deterioration has not been clearly elucidated yet. Nafion is the membrane developed by DuPont, in which hydrophilic perfluoroalkyleneether sidechains terminated with  $-\text{SO}_3\text{H}$  are periodically attached to the hydrophobic fluorocarbon backbone and widely used for PEFCs. Despite numerous studies, the structure of Nafion is still subject to controversy and several models have been proposed. The water molecules are known to play key roles for the membrane to show high ion conductivity and for the cell to maintain its performance under operation. Extensive efforts have been made in terms of modelling water transport and its management.

The properties of the membranes have been extensively investigated by  $^1\text{H}$  NMR spectroscopy in terms of modelling water transport and its management [4-10].  $^1\text{H}$  NMR spectra of water molecules adsorbed on solid materials often sensitively reflect the characteristics of the underlying materials [11-13]. Recently by observing the change of  $^1\text{H}$  NMR signals of water confined in Nafion 112, we found that the membrane underwent a characteristic morphological change on heating at 358 K. The morphology was thermally converted so that the mobility of the confined water molecules became higher and the chemical environments became more homogeneous, which would enable the higher proton conductivity of the membrane. The morphology was retained even after the temperature reverted to 297 K for fairly long time [14]. On the other hand, the chemically deteriorated membranes by OH radicals produced in Fenton media did not undergo such morphological change [15]. Due to the loss of the sulfonic acid groups of Nafion and/or the decomposition of the C-F bonds by the attack of OH radicals [16], the polymer could not take the morphology in which water molecules are highly mobile to enable the high conductivity. Consequently, the proton conductivity would fall during the practical operation of PEFCs.

Although the polymer electrolyte membranes employed for PEFCs show superior conductivity in the wet state, they deteriorate when they are dry or under low humidified conditions during operation. Therefore, water managements to protect the membranes from drying are a major concern during fuel cell operations.

In the present study, it was indicated that the  $^1\text{H}$  NMR spectra of water confined in the less humidified membranes showed characteristic feature different from those in hydrated membranes, which is associated with the change in the morphology of the membranes. By observing the  $^1\text{H}$  NMR spectral changes of the water, it was deduced that the polymer could

take distinct morphologies depending on temperatures and humidified conditions and that the conversion among them could be significantly slow below 348 K. A plausible scheme of the local conversion of the states of the water molecules associated with the morphological changes of the polymer was proposed.

## 2. Experimental

Commercially available Nafion 112 membranes (E. I. duPont de Nemours and Co.) were used as received. Although several pre-treatments of the membranes have been recommended [17], some steps significantly affected the spectral features. Therefore, we measured the membranes without any pre-treatment. The  $^1\text{H}$  NMR spectra of the membranes were measured in the form of a single sheet. For the measurements of temperature dependence of the water signals, a membrane sheet of 2 x 50 mm was located in a 3 mm o.d. (55 mm high) glass NMR sample tube, which was capped and carefully sealed with Teflon films to keep it airtight.

$^1\text{H}$  NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz in the temperature range of 298-348 K without sample rotation. The spectra were obtained after Fourier transformation of the FID signals following a single pulse excitation with pulse duration of 3.0  $\mu\text{s}$  and a 5 s relaxation delay. To eliminate the background signal of the NMR probe, the spectrum measured with an empty NMR sample tube was subtracted from all the spectra. Chemical shifts were measured relative to DSS (sodium 2, 2-dimethyl-2-silapentane-5-sulfonate) as an external reference.

## 3. Results and Discussion

### 3.1. Membrane dehydration

The  $^1\text{H}$  NMR spectrum of water molecules in a hydrated Nafion 112 membrane in the form of a single sheet presented broad resonance lines as shown in Fig. 1 (a) at 298 K. The resonance line is apparently broadened by the distribution of chemical shifts of the water with different structures and mobility in the chemically different environments in the membrane [14]. The heterogeneity of the signals of the water molecules suggests the heterogeneity of the polymer morphology and/or structure. Under humid conditions, the morphology of the hydrated Nafion is considered to be stable at room temperature. However, although Nafion is known to possess exceptional thermal, chemical and mechanical stability, it has been acknowledged that it showed sometimes different properties after the long term storage [18].

Actually when the received sample was kept under less humid conditions for a long time, the membrane showed sometimes a quite different spectral feature, which was composed of three regions spread over the wide range of the chemical shifts as shown in Fig. 1 (b). The partial dehydration of the membrane might take place and the polymer morphology became more heterogeneous to lead such a spectral feature of water molecules. This would be supported by the following facts; after heating the hydrated membrane for 4 h in an open system at 348 K, the signal was barely observed due to the evaporation of the water confined in the membrane.

After kept the membrane under the ambient temperature and humidity for 15 h, the water molecules in the air were reabsorbed in the membrane and the signal intensity recovered by 85 % of that before heating. However, as shown in Fig. 1 (c) the membrane did not show a spectrum like that for the initial hydrated membrane but showed a spectrum consisting of three distinct regions similar to Fig. 1 (b). Thus the spectral features are suspected to be characteristic of the waters in the less humidified membranes.

### *3.2 Humidification of the dried membrane*

Then we soaked the membrane in pure liquid water for 24 h at room temperature and wiped excess water on the surface and measured the  $^1\text{H}$  NMR spectrum. The membrane must contain enough amount of water. However, as shown in Fig. 1 (d), the spectrum did not revert to that of the initial hydrated membrane (Fig. 1 (a)) and presented still three distinct regions although the low field region was notably enhanced after the addition of water. This fact suggests that on getting into less hydrated states, the morphology of the polymer should be converted to more heterogeneous one than that of the hydrated membrane, which must be considerably stable at room temperature not to revert to the initial morphology of the hydrated membrane at least 24 h even after the addition of enough amount of water.

From the contrast variation method combined with the SANS (small angle scattering with neutrons) technique, Rubatat et al. have recently reported that the structure between 10 and 1000 Å of the Nafion could be described in terms of elongated polymeric aggregates connected at larger scale to form a film with good mechanical properties. The water swelling process allows separating these aggregates following two different regimes depending on the hydration; a lamellar dilution at low water content and 2 D swelling for polymer volume fraction higher than 60 % [19]. On the other hand, Gebel proposed the swelling mechanism which involves structural reorganization characterized by a cluster number decrease and an intercluster distance increase. A conversion from isolated cluster to percolation structure occurs in the swelling process and from percolation to isolated cluster structure in the dehydration process. He stated that the structural evolution from dry to highly swollen membrane requires a large amount of thermal energy to permit the necessary polymer

reorganization. The evolution induced at high temperature is not reversible at room temperature [20]. Our observation may support his statement.

### 3.3 *Thermal conversion*

#### 3.3.1 *Rapid conversion*

Therefore, we heated the membrane which contains enough amount of water but is assumed to retain the morphology of less hydrated membrane showing the spectrum of Fig. 1 (d). Actually, after the membrane was heated at 348 K for 1 h under airtight conditions, the spectrum became similar to that of the hydrated membrane (Fig. 2 (b)) although the signal was rather broader. The temperature was kept at 348 K for another 1 h, but no significant change was observed (Fig. 2 (c)). Then the temperature was decreased to 328 K. On keeping the temperature at 328 K long time enough (about 27 h), the spectral feature did not show significant change although the peak became little bit broader and shifted to the down field. On further decrease of temperature to 298 K, notable difference in the spectrum was not observed as compared to that at 328 K although further down field shift was observed. Thus on heating the dehydrated membrane along with the addition of water, the polymer apparently became to take a similar morphology as that of the hydrated membrane.

#### 3.3.2 *Slow conversion via transient state*

However, it is noted that after keeping the sample under the air tight condition at 298 K for a long time (18 days), the signal became significantly sharp as shown in Fig. 2 (e). The peak area did not change but it shifted to the upfield and the line width became 1/3 of that measured 18 days ago. This fact suggests that the attained morphology (or state) just after heating at 348 K is not exactly the same as that of the initial hydrated membrane although the apparent spectral feature was similar. The morphology was not stationary but transient one and converted to a more homogeneous one very slowly, as deduced from the sharp line width and high field shift. Namely, the sharp line width would indicate the mobility gained and high field shift may mean the weakened hydrogen bonding among the interacting water molecules.

As reported previously, on heating a hydrated membrane at 358 K under airtight conditions for 30 min, the resonance line width was reduced to 1/3, which was retained more than 18 days at 297 K after the temperature reverted to 297 K [14]. This characteristic change was attributed to the morphological change of the polymer, so that the chemical environments of

water became homogeneous and/or chemical exchange among water molecules became rapid. The attained polymer morphology is highly stabilized, most probably by the interaction with water molecules [14]. However, on initial heating lower than 348 K, the line width reverted to that before temperature increase, suggesting that the morphological conversion to a highly homogeneous state should not take place by heating the membrane below 348 K. The attained morphologies after heating at 348 K and 358 K may not be exactly the same but the both morphologies are evidently more homogeneous as compared to that of the hydrated membrane before heating. At around 348 K a certain local conversion must be triggered off in the polymer, and a very slow morphological conversion would be initiated to proceed, in which water molecules are involved.

### *3.4 A scheme of the morphological conversions*

The present results demonstrate that the change of the water properties on heating and dehydration of the membrane are closely associated with the conversion of the polymer morphology. Although the direct feature of the polymer morphology could not be provided, a plausible conversion scheme suspected from the change of water states is proposed in Fig. 3.

We designated here, the initial hydrated state as A, partially dried state as B, water saturated state after drying the membrane as B', transient state after heating B', as A', and highly homogeneous hydrated state as C.

#### *3.4.1 Conversion from A to B*

Under humid conditions, the morphology of the hydrated membrane is considered to be stable at room temperature (state A). As water molecules evaporate, the polymer would become to take less homogeneous morphology (state B) to provide a  $^1\text{H}$  NMR spectrum of water molecules composed of three regions. It was reported that in isothermal dehydration, with a decrease of the water content, the percolation structure of the polymer was converted into the isolated cluster structure, together with an increase of length or even closure of the intercluster channels [21].

Owing to the shortage of the bulk water, the pendant group moiety would become more rigid and the segmental motion would become more restricted. Accordingly, the mobility of the water molecules around the distinct segments (hydrophilic sulfonate groups, and hydrophobic fluorocarbon main and side chains) would become more restricted and the chemical exchange of the water molecules inter the distinct segments would become slower, resulted in the wider distribution of the chemical shift and broadening of the signals.

The spectra of Fig. 1 (b)-(d) comprise of three distinct regions over 10 ppm, (i) 9-13 ppm, (ii) 7-9 ppm, and (iii) 3-6 ppm. Although the membranes contain considerable amount of water, the spectral features are rather similar to  $^1\text{H}$  MAS NMR spectra of dried Nafion reported by Zhang et al., which consist of separated regions over 14 ppm [10]. The peak near 10 ppm

was assigned to hydrogen ions associated with the sulfonate group in hydrogen-bonded clusters [4]. They stated that the smaller average shift may result from the presence of hydration that is difficult to remove. A broad peak ranging from 5.5 to 9 ppm was assigned to hydrogen ions and water in the ionic clusters undergoing exchange with each other.

As shown in Fig. 1(d), the peak area of the lowest region of the spectrum was notably enhanced after the addition of water to the less hydrated membrane. Since the water added from outside would initially access to the hydrophilic part of the polymer, the lowest field region at around 9 ppm could be reasonably ascribed to the signals of the water in the vicinity of the sulfonate groups, which is consistent with the assignment by Zhang et al. [10].

They ascribed the peak at around 3.5 ppm to water physically sorbed or trapped in either the side chain or the backbone environments. By measuring the IR spectra of H<sub>2</sub>O, D<sub>2</sub>O and HDO in hydrated Nafion membranes, Falk reported that a substantial proportion of water molecules appeared to have an OH group (or occasionally both OH groups) exposed to the fluorocarbon environment [22]. However, since the peak around at 3.5 ppm in Fig.1 (b) and (c) is larger than that for the water molecules in the vicinity of the sulfonate groups (at around 9 ppm), it seems too large to be ascribed to water physically sorbed or trapped in either the side chain or the backbone environments. We are planning to identify the signals by measuring the water molecules confined in perfluorinated ionomers with various length of main and side chains.

#### 3.4.2 *Slow or no conversion from B' (B with water saturation) to A*

The morphology of the less hydrated state B must be quite stable at room temperature, since three regions hold in the spectrum after soaking the membrane in pure water for 24 h (state B'). The morphological state B' would not be easily converted to the morphological state A, unless providing a high amount of thermal energy for the necessary polymer reorganization, as Gebel pointed out [20].

#### 3.4.2 *Thermal conversion from B' to transient state A'*

Actually on heating at 348 K, the morphological conversion takes place and the water molecules around the hydrophilic part diffuse gradually into the other domains, which would enhance the chemical exchange of the water protons among the distinct domains, leading to the higher mobility of the side chains giving the similar NMR spectrum (state A') as the initial water swollen membrane (state A).

#### 3.4.3 *Slow conversion from A' to homogeneous state C*

The morphology of polymer membranes in the hydrated state A is considered to be stable under humid conditions although the morphology is not highly homogeneous as deduced from the chemical shift distribution of the NMR signal [14]. For Nafion in the hydrated state, a structural model of cylindrical or ribbon like polymeric aggregates surrounded by the ionic groups and the water molecules has been recently proposed on the basis of the data on

small-angle X ray and neutron-scattering measurements [19]. On increase of temperature up to 348 K, such polymeric aggregates may resolve slowly and the further morphological conversion would proceed very slowly via transitional state A' until attaining to the highly homogeneous state C. In this procedure, the bulk water would spread over the whole membrane, which enables the rapid chemical exchange among the water molecules in the whole membrane and consequently the mobility of water molecules is enhanced, resulting in the reduction of the line width of the water signal. These procedures are very slow, but accelerated at the temperature higher than 358 K. It would take less than 30 min at 358 K to complete the conversion. However, when the initial temperature increase was below 348 K, the water peak became as broad as that before temperature increase shortly after the temperature was decreased back to 298 K, indicating that the conversion from A to C would not occur below 348 K [14]. Thus, to resolve the aggregates to the highly homogeneous state sufficient energy must be provided by elevating the temperature up to the critical value of 348 K, at which the conversion must be triggered off.

The bulk water must play also an important role to attain the homogeneous state, since the conversion to state C did not take place under less humidification conditions even at 358 K [14]. The heterogeneity of the morphology and mobility of water molecules and the membrane in distinct states are summarized in Table 1 along with the corresponding  $^1\text{H}$  NMR spectra presented in Figs. 1 and 2.

Although the detailed mechanism of the proton transport and the exact role of water in the membrane-proton interaction have not been clarified yet, the ionic conductivity of the membrane is reported to be closely related to the mobility of the water molecules in the membranes [23]. Since the state C must be favoured to achieve the high ionic conductivity, the pre-treatment of the membranes or the PEFC systems above 348 K (favourably above 358 K) under humidified conditions, would improve the efficiency in the performance for the practical operation of PEFCs.

It is well known that during the actual operation of PEFCs, the conductivity falls and the membrane is deteriorated when the membranes are dry or under low humidified conditions. In this case, the morphological change to state B is suspected to take place. Since for state B water molecules are localized at distinct regions, the conductivity must decline and the polymer might be vulnerable to the direct attack by active oxygen species such as OH radicals and/or  $\text{H}_2\text{O}_2$  formed during operation. The bulk water may play a role to protect the membrane from the direct attack. Furthermore, the morphological states A and C may be preferable organizations against the attack.

Thus, the spectral changes obviously demonstrated that the polymer could undergo various morphological changes at different temperature and hydrated states, and for some cases the

conversion was extremely slow. Therefore, careful attention should be paid whether the polymer is in a morphologically stationary state or a transitional state on investigation of the properties of the membrane. Although the present results are preliminary, the more detailed features of the morphological conversion are under investigation in our laboratory by observing the  $^1\text{H}$  NMR spectra of water confined in the membranes at various temperatures and hydrated conditions.

#### **4. Conclusions**

Perfluorinated ionomer membranes are widely used for polymer electrolyte fuel cells. The morphology and properties of the membranes have been intensively investigated to correlate the performance and deterioration of PEFCs. For the achievement of the sufficient performance on the practical operations and the development of novel membranes, both detailed and accurate information are required. In the present study, by observing the  $^1\text{H}$  NMR spectral changes of water molecules confined in the polymer membranes under various conditions, it was deduced that the polymer undergoes very slow morphological change among distinct states depending on the hydrated states and temperatures below 348 K, while the conversion to the highly homogeneous morphological state could be achieved relatively fast (less than 30 min) at 358 K under humidification conditions. Such slow morphological changes can influence accurate investigations of the properties of the polymer membranes and the evaluation of the performance of the fuel cells. Therefore, it would be desirable to recognize whether the polymer membrane is in a morphologically steady or a transient state under the investigations concerned. The characteristic  $^1\text{H}$  NMR spectral change of the water could help identify the morphological states to some extent, which might be difficult with the other alternative techniques.

#### **Acknowledgement**

The authors are grateful to Mr S. Watanabe and Mr I. Toyoda for their cooperation and helpful discussion. This work was supported by Research and Development of Polymer Electrolyte Fuel Cells from New Energy and Industrial Technology Development Organization (NEDO), Japan.

#### **References**

- [1] K.-D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster, *Chem. Rev.* 104 (2004) 4637.
- [2] O. Savadogo, *J. Power Sources* 127 (2004) 135.

- [3] K. Miyatake, M. Watanabe, *Electrochemistry* 73 (2005) 12.
- [4] J. N. Bunce, S. J. Sonderheimer, C. A. Fyfe, *Macromolecules* 19 (1986) 333. [5] Y. S. Pak, G. Xu, *J. Electrochem. Soc.* 140 (1993) 1237.
- [5] Y. S. Pak, G. Xu, *J. Electrochem. Soc.* 140 (1993) 1237.
- [6] B. MaMillan, A. R. Sharp, R. L. Armstrong, *Polymer* 40 (1999) 2471.
- [7] J. R. P. Jayakody, A. Khalfan, E. S. Mananga, S. G. Greenbaum, T. D. Dang, R. J. Mantz, *J. Power Sources* 156 (2005) 195.
- [8] G. Ye. N. Janzen, G. R. Goward, *Macromolecules* 39 (2006) 3283.
- [9] J-C. Perrin, S. Lyonnard, A. Guillermo, P. Levitz, *P. J. Phys. Chem. B* 110 (2006) 5439.
- [10] M. V. Giotto, J. Zhang, P. T. Inglefield W.-Y. Wen, A. A. Jones, *Macromolecules* 36 (2003) 4397.
- [11] A. Y. Nosaka, E. Kojima, T. Fujiwara, H. Yagi, H. Akutsu, Y. Nosaka, *J. Phys. Chem. B* 107, (2003) 12042.
- [12] A. Y. Nosaka, T. Fujiwara, H. Yagi, H. Akutsu, Y. Nosaka, *J. Phys. Chem. B* 108 (2004) 9121.
- [13] A. Y. Nosaka, T. Fujiwara, T. Ikegami, H. Yagi, H. Akutsu, Y. Nosaka, *J. Phys. Chem. B* 110 (2006) 8380.
- [14] A. Y. Nosaka, S. Watanabe, I. Toyoda, Y. Nosaka, *Macromolecules* 39 (2006) 4425.
- [15] A. Y. Nosaka, S. Watanabe, I. Toyoda, Y. Nosaka, *Electrochemistry (Special Issue for Fuel Cells)* 75 (2007) 137.
- [16] T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umebayashi, A. Tasaka, Y. Iriyama, T. Abe, Z. Ogumi, *J. Power Sources*, 158 (2005) 1222.
- [17] N. Yoshida, T. Ishisaki, A. Watakabe, M. Yoshitake, *Electrochim. Acta* 43 (1998) 3749.
- [18] H. L. Yeager, A. Steck, *J. Electrochem. Soc.* 128 (1981) 1880.
- [19] L. Rubatat, A.-L. Rollet, G. Gebel, O. Diat, *Macromolecules* 35 (2002) 4050.
- [20] G. Gebel, *Polymer* 41 (2000) 5829.
- [21] V. Freger, E. Korin, J. Wisniak, *J. Membr. Sci.* 160 (1999) 213.
- [22] M. Falk, *Can. J. Chem.* 58 (1980) 1495.
- [23] S. J. Paddison, R. Paul, T. A. Zawodzinski, Jr, *J. Electrochem. Soc.* 147 (2000) 617.

**Table 1 States of water and membranes under different hydrated conditions, and corresponding  $^1\text{H}$  NMR spectra measured at 298 K.**

	<b>Hydrated State of Membrane</b>	<b>Structure and Mobility of Water/Membrane</b>	<b><math>^1\text{H}</math> NMR Spectra of Water</b>
<b>A</b>	<b>hydrated</b>	<b>less homogeneous/stationary</b>	<b>Figure 1 (a)</b>
<b>A'</b>	<b>hydrated</b>	<b>less homogeneous/transitional</b>	<b>Figure 2 (d)</b>
<b>B</b>	<b>less hydrated</b>	<b>inhomogeneous</b>	<b>Figure 1 (c)</b>
<b>B'</b>	<b>hydrated</b>	<b>inhomogeneous</b>	<b>Figure 1 (d)</b>
<b>C</b>	<b>hydrated</b>	<b>highly homogeneous</b>	<b>Figure 2 (e)</b>

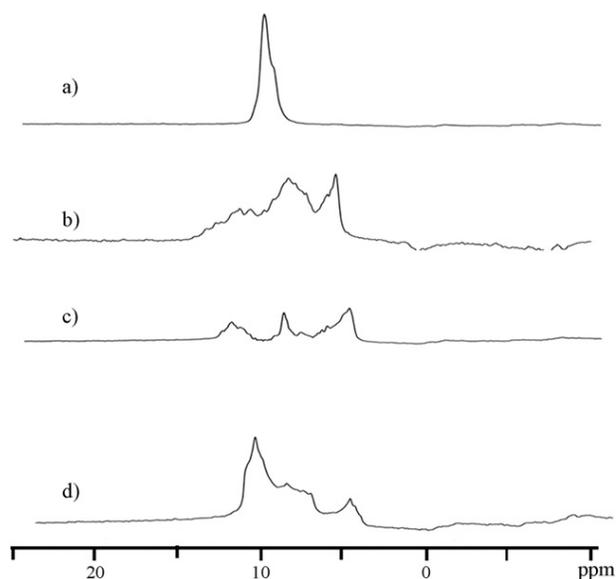


Fig. 1.  $^1\text{H}$  NMR spectra of Nafion membranes, measured at 500 MHz at 298 K, (a) hydrated Nafion 112, (b) the sample kept at room temperature under ambient conditions for 3 months, (c) the sample heated for 4 h at 348 K, and then kept under ambient conditions at room temperature for 15h (d) measured after the sample (c) was soaked in pure water at room temperature for 24 h then wiped excess of water on the surface with a paper.

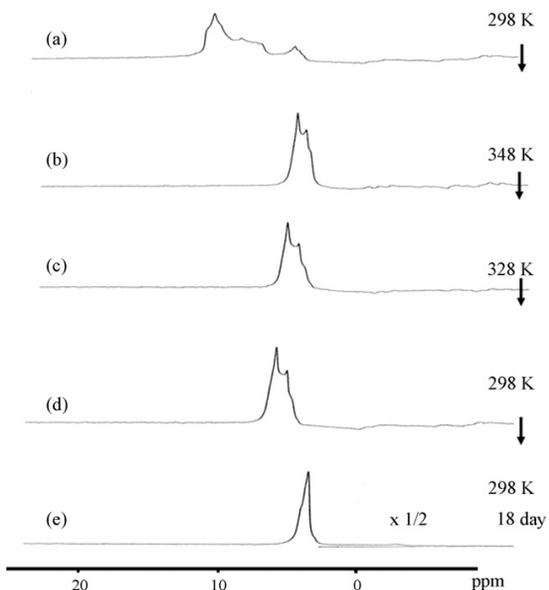


Fig. 2. The temperature dependence of  $^1\text{H}$  NMR spectra of water molecules confined in Nafion 112 (sample (d) in Fig. 1), measured under air tight conditions at (a) 298 K, The temperature was increased at the rate of 10 K/5 min to 348 K, and the temperature was kept for (b) 2 h. Then the temperature was decreased at the rate of 10 K /30 min to 328 K and kept for (c) 27 h. Afterwards, the temperature was decreased to 298 K and kept for (d) 15 min. The sample was kept at room temperature for 18 days and measured (e) at 298 K.

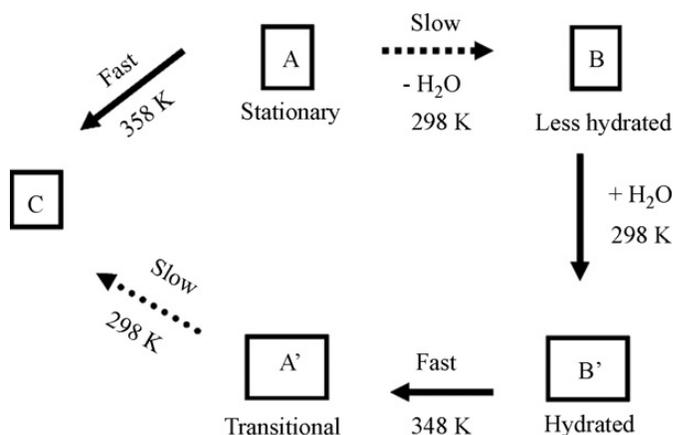


Fig. 3. A plausible conversion scheme among distinct morphologies of Nafion 112 membranes at different temperatures and hydrated states deduced from  $^1\text{H}$  NMR spectra of the confined water molecules.