The state of water in the series of sulfonated poly (phthalazinone ether sulfone ketone) (SPPESK) proton exchange membranes

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ABSTRACT

The different states of water in a series of SPPESK membranes, including sulfonated poly (phthalazinone ether sulfone ketone) (SPPESK) membrane, cross-linked (XL) SPPESK membrane and SPPESK/polyacrylic acid (PAA) semi-interpenetrating polymer network (sIPN) membrane were investigated by low temperature differential scanning calorimetry (DSC) measurements. Only one melting peak was observed for each DSC curve, therefore the free water cannot be distinguished from freezing bound water in the experimental condition. The melting temperature of the freezable water was found to decrease when the content of the freezable water reduced. The content of non-freezing bound water decreased with the increase in total water uptake in each type of the membranes. It indicates that the total water uptake cannot exactly reveal the ability of tight water retention of the membranes. As compared with SPPESK/PAA membrane, SPPESK and XL-SPPESK membranes presented a higher ability of water retention because of higher content of non-freezing bound water measured. A schematic structural model is given to explain the interrelation of distribution of ionic groups (hydrophilic groups) and structure of polymers to the content of non-freezing bound water.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a promising power force for electric vehicles due to its fast startup ability and environmental friendship [1–5]. Since the hydration of the proton exchange membranes (PEMs) is necessary for the properties of proton conductivity, water retention and dimensional stabilities, etc., the state of water in the PEMs is extremely important for the operation of PEMFCs. For example, during the fuel cell operation, non-freezing bound water is more likely to be retained in the membranes because of its strong interaction with the polymer matrix, so that the content of which has great related to the startup speed or the electrical property especially at high/low temperature (<0 °C or >100 °C) [6]. Although many studies have been done on the total water uptake of the hydrated PEMs [7–10], the different states of water in the total water uptake are still necessary to be investigated.

In the hydrated polymers, based on the analysis by several techniques such as IR, H NMR and DSC measurements, three types of water namely non-freezing bound water, freezing bound water and free water are commonly defined according to the interaction between water and polymers [11–14]. Non-freezing bound water is the water strongly associated to ionic and polar sites of the polymer chains and has no detectable phase transition from −73 °C to

0 °C. Freezing bound water has weak interaction with the polymer matrix and lower phase transition temperature than 0 °C. Free water is defined as the water which has the same phase transition temperature as the bulk water (around 0 °C), therefore it almost has no interaction with the polymer matrix. In some cases in literatures there was only one melting peak observed through DSC measurement, in which freezing bound water and free water are denoted as freezable water [6,13,14].

In our previous work, a series of poly (phthalazinone ether sulfone ketone) (PPESK) membranes, including sulfonated PPESK (SPPESK) membrane, amide cross-linked SPPESK (XL-SPPESK) membrane and SPPESK/polyacrylic acid semi-interpenetrating polymer network (SPPESK/PAA sIPN) membrane were prepared [15–20]. The total water uptake of the PEMs and its effects on properties such as proton conductivity, dimensional stability and mechanical strength were examined carefully. The present work focus on the different interaction between water and the SPPESK membranes. It is found that the structure of polymers and distribution of the ionic groups in the hydrated membranes strongly influence the state of water in the membranes.
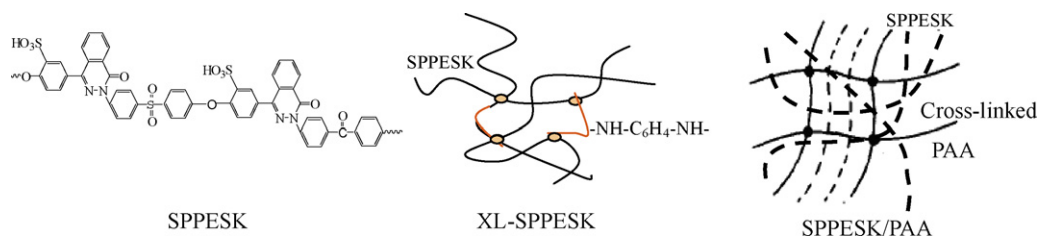
2. Experimental

2.1. Preparation of the series of SPPESK membranes

The series of SPPESK membranes were prepared in our laboratory. Sulfonation of PPESK was performed through a heterogeneous

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Scheme 1. The structure of the series of SPPESK membranes.

method with fuming acid as sulfonated agent in the solvent of chloroform [16]. SPPESK was cross-linked by adding p-phenylene diamine/dimethylacetamide (DMAc) dropwise to the solution of SPPESK/DMAc in order to increase the swelling resistance of the SPPESK membranes [17]. SPPESK/PAA sIPN was prepared by the *in situ* free radical polymerization of acrylic acid (AA) in the SPPESK/N-methyl-2-pyrrolidone (NMP) solution [18,19]. The obtained series of SPPESK materials then underwent procedure of solution evaporation on a glass sheet to prepare the final membranes. Then the membranes were carefully peeled from the glass and dried in vacuum at 120 °C overnight to get the dry membrane samples. Water resistance was increased in the XL-SPPESK and the SPPESK/PAA membranes due to the covalent cross-linking with diamine or entanglement of the SPPESK and PAA chains each other. High proton conductivity was gained in the SPPESK/PAA membrane because the carboxyl groups together with the sulfonic acid groups acted as the proton conducting groups of the membrane. Chemical structures of the three kinds of SPPESK membranes are shown in Scheme 1.

2.2. Total water uptake of the membranes

The SPPESK membranes were measured of their total water uptake. The freshly prepared dry membrane samples were weighted and immersed into the distilled water. The weight of the wet membrane was measured several times until their weight remained constant (fully hydrated), which took about 24 h. Then the fully hydrated membrane was wiped with tissue paper and weighted again. Water uptake of the membranes was calculated from the weight difference between wet (w_{wet}) and dry (w_{dry}) membrane reference to the weight of the dry specimen:

$$\text{Total water uptake}\,(\%) = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100\% \qquad (1)$$

2.3. Measurement of state of water in the membranes

The state of water in the membranes was investigated through the method of differential scanning calorimetry (DSC METTER TOLEDO DSC822). Immediately after the measurement of the water uptake of the membrane, the fully hydrated membrane sample was sealed in a DSC sample pan. Two different methods were used in the experimental. The first one is a slow cooling and heating cycle measurement, in which the sample was first cooled from 25 °C to −50 °C at a rate of 2 °C/min, and then heated at the same rate up to 50 °C. The second one is a fast cooling and heating cycle measurement, in which the sample was jumped to −50 °C inside the DSC chamber, and then heated up to 50 °C at a rate of 5 °C/min. The content of freezable water is defined as the endothermic peak area (A_{endo}) of the hydrated membrane at around 0 °C divided by the melting endothermic heat of fusion of pure water (334 J/g), reference to the total weight of water (w_{water}) in the sample. Here the total weight of water refers to the weight difference between wet and dry membrane. Since in the present experiments freezing bound water cannot be distinguished from free water, they both

were denoted as freezable water.

$$\text{Freezable water}\,(\%) = \frac{A_{endo}}{334 \times w_{water}} \times 100\% \qquad (2)$$

The content of non-freezing bound water in the hydrated membrane was then calculated by the following equation:

$$\text{Non-freezing bound water}\,(\%) = 100\% - \text{Freezable water}\,(\%) \qquad (3)$$

3. Results and discussion

3.1. Types of water in the series of SPPESK membranes

The DSC curve of the SPPESK/PAA membrane in the slow cooling and heating cycle measurement is shown in Fig. 1. At a rate of 2 °C/min of heating up (it is a rate of heating up in common use), only one melting peak was observed in the heating up process, which indicates that free water cannot be distinguished from freezing bound water in the experimental condition. It was the same case for SPPESK and XL-SPPESK membranes and was typical for polymers reported in literatures [6,13,14]. The reason is mainly related to the relatively high rate of cooling or heating as compared with the thermal process of water in polymers. Henceforth freezable water was used to represent the freezing bound water and free water. The fast cooling and heating cycle measurement was performed at the following experiments to investigate the thermal process of the hydrated SPPESKs membranes.

The DSC curves of the series of SPPESK membranes with different contents of freezable water in the fast cooling and heating cycle measurement is shown in Fig. 2. Here XL-SPPESK 70.4% denoted as the XL-SPPESK membrane with the content of freezable water of 70.4%, henceforth. For each type of the XL-SPPESK membranes and SPPESK/PAA membranes the melting temperature of the freezable water (signed in Fig. 2) was found to be decreased as the
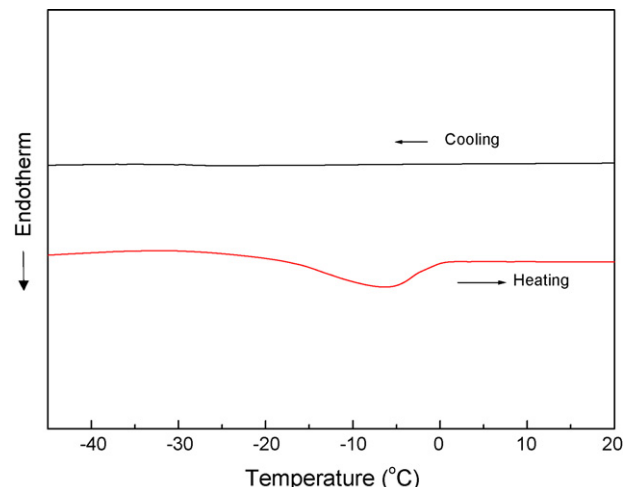
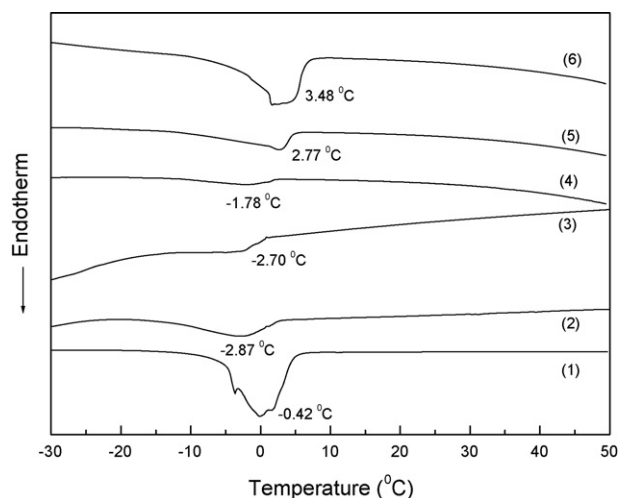**Fig. 1.** Cooling and heat cycle DSC curve of SPPESK/PAA membrane.

Fig. 2. Heating up DSC curves of SPPESK series membranes with different contents of freezable water.

content of the freezable water decreased. The lower melting temperature implies the increased interaction between water and the polymer matrix. As compared with the XL-SPPESK and SPPESK/PAA membranes, it can be seen that water in the XL SPPESK membrane has lower melting temperature, which is evidence that XL-SPPESK membrane can hold water more tightly than that of the SPPESK/PAA membrane.

3.2. Non-freezing bound water via total water uptake

The content of non-freezing bound water via the total water content in the series of the SPPESK membranes is illustrated in Fig. 3. In each type of the SPPESK membranes the content of non-freezing bound water decreased with the increase in the total water uptake. Among the different types of water in polymers, non-freezing bound water has the strongest interaction with the polymer matrix and is more likely to be retained in the membranes. Therefore high content of non-freezing bound water is related to the ability of water retention. The decreasing trends of non-freezing bound water with the increasing total water uptake in the series of SPPESK membranes indicates that the total water uptake of the membranes cannot exactly reveal the ability of tight water retention of the membrane. When the membranes contained approximately the same total amount of water as can be seen in
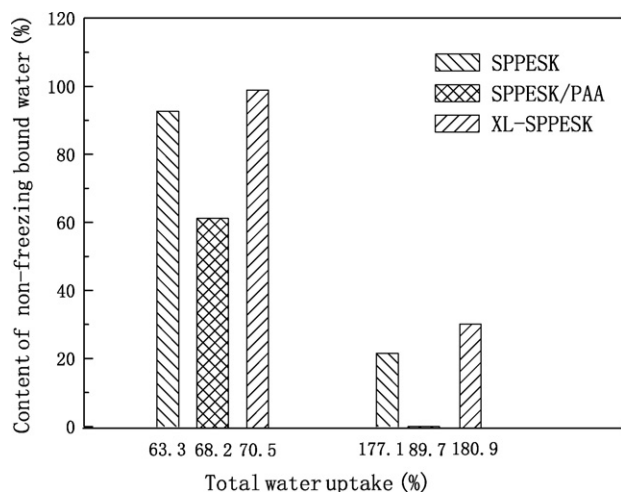

Fig. 3. Content of the non-freezing bound water in the series of SPPESK membranes.

Table 1
The state of water in hydrated SPPESK series membranes.

Sample number	Samples	Total water uptake (%)	Non-freezing bound water content in total water uptake (%)
1	SPPESK-DS0.9	63.3	92.6
2	SPPESK/PAA-DS0.86–0.83	68.2	61.7
3	SPPESK-DS1.2	177.1	21.5
4	XL-DS1.5–25%	180.9	29.6

Fig. 3, XL SPPESK membranes had the highest value of non-freezing bound water content and SPPESK/PAA membranes had the lowest value.

It is known that several factors may influence the state of water in a hydrated membrane, such as concentration and distribution of the ionic groups, structure of the polymers etc. To make it clearly, the proportion of the non-freezing bound water in the total water uptake of the different membranes is summarized in Table 1. It can be seen that the SPPESK membrane had the higher content of non-freezing bound water than that of the SPPESK/PAA membrane through sample numbers 1 and 2, irrespective of the approximately total water uptake of them. Here SPPESK/PAA-DS0.86–0.83 refers to the SPPESK/PAA membrane with the sulfonation degree (DS) of SPPESK 0.86 and the ratio of SPPESK 0.83 g/g. Although DS in the SPPESK membrane was closed with that of the SPPESK/PAA membrane, there were much more ionic groups in the SPPESK/PAA membrane because of the large numbers of hydroxy of PAA. However, the lower content of non-freezing bound water of SPPESK/PAA membrane indicates that besides the concentration of ionic groups there are some other important factors such as distribution of the ionic groups and structure of the polymers, which have great related to the content of non-freezing bound water. XL-DS1.5–25% refers to the cross-linked SPPESK membrane, in which the initial DS of SPPESK was 1.5 and the content of cross-linker was 25% of the sulfonated acid group of the SPPESK. Assuming the cross-linking degree was about 80% (it was detected in the previous work [17]), the concentration of ionic groups was approximate in both XL-SPPESK and SPPESK membranes. It is shown in Table 1 that the XL-SPPESK membrane had a slightly higher content of non-freezing bound water than that of the SPPESK membrane through sample numbers 3 and 4, although the total water uptake and the concentration of sulfonic acid groups in both membranes were nearly the same.

3.3. Structural model of hydrated membranes

Fig. 4 illustrates a schematic model of the distribution of ionic groups and the structure of the hydrated SPPESK membranes. In the SPPESK and XL SPPESK polymer chains, sulfonic acid groups are pendent on the hydrophobic polymer chains, which typically assemble into nano-size clusters [1] and likely hold water tightly (Fig. 4A). As compared with SPPESK membrane, XL PPESK membranes had a slightly higher content of non-freezing bound water, although there was nearly the same concentration of sulfonic acid in the two types of membranes (as illustrated in Table 1). It implies that cross-linking made the SPPESK chains denser, which would be related to the smaller nano-size clusters therefore the tighter hold of water. Different from the SPPESK and XL SPPESK membranes, in the SPPESK/PAA membranes the SPPESK and PAA chains were entangled with each other, which resulted in the extremely homogeneous dispersion of ionic groups and water (Fig. 4B). However, the lower non-freezing bound water content in the SPPESK/PAA illustrates that this homogeneous dispersion of ionic groups (hydrophilic groups) has less ability of bounding water tightly than the nano-size clusters of the SPPESK and XL SPPESK membranes.
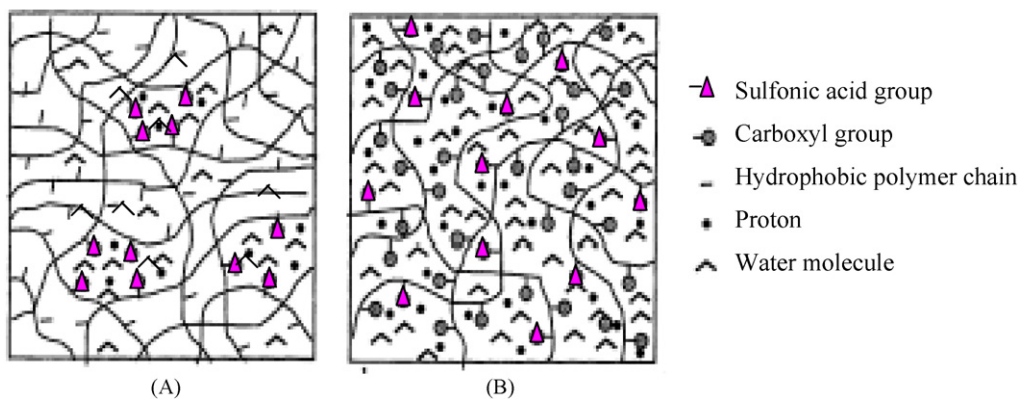
Fig. 4. Schematic picture of the morphology of hydrated membranes.

4. Conclusions

The series of SPPESK membranes was prepared and tested of their state of water through the method of DSC. There was only one melting peak observed in the heating up DSC curves, which indicates the free water cannot be distinguished from freezing bound water in the experimental condition. The melting temperature of the freezable water was found to decrease as the content of the freezable water reduced. As compared with SPPESK/PAA membrane, higher content of non-freezing bound water was measured in the XL-SPPESK membrane, which indicates higher ability of water retention. A schematic structural model of the hydrated membranes illustrates the interrelation of the state of water to the distribution of the ionic groups and the structure of the polymer chains in the hydrated membranes. The homogeneous dispersion of ionic groups (hydrophilic groups) in SPPESK/PAA membrane has less ability of bounding water tightly than the nano-size clusters of the SPPESK and XL SPPESK membranes.

Acknowledgements

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