

Short communication

## Conductivity of aromatic-based proton exchange membranes at subzero temperatures

Junbo Hou<sup>a,b</sup>, Hongmei Yu<sup>a,\*</sup>, Liang Wang<sup>a,b</sup>, Danmin Xing<sup>a</sup>,  
Zhongjun Hou<sup>c</sup>, Pingwen Ming<sup>c</sup>, Zhigang Shao<sup>a</sup>, Baolian Yi<sup>a</sup>

<sup>a</sup> Fuel Cell R & D Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
457 Zhongshan Road, Dalian 116023, PR China

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

<sup>c</sup> Sunrise Power Co. Ltd., 1 Huojia Road, Dalian 116025, PR China

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### Abstract

Stable proton exchange membrane (PEM) with good proton conductivity at subzero temperatures is important for the development of PEM fuel cell cold start. In this work, subfreezing conductivity was reported for several aromatic-based PEMs including sulfonated polyimides (SPIs) with three values of ion-exchange capacity (IEC), sulfonated poly(ether ether ketone) (SPEEK) and disulfonated poly(arylene ether sulfone) copolymer (SPSU) as well as Nafion<sup>®</sup> 212. Measurements were performed using the electrochemical impedance spectroscopy (EIS) technique. The results showed that only fully hydrated SPEEK (IEC, 1.75) and SPSU (IEC, 2.08) had comparable conductivities with Nafion<sup>®</sup> 212 at subzero temperatures. Considering implement of gas purge before subzero storage of PEM fuel cell, the conductivity for those PEMs humidified by water vapor at activity of 0.75 was also investigated. The state of water in aromatic-based PEMs was quantified by differential scanning calorimetry (DSC), and its correlation with conductivity of the membrane was also discussed.

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**Keywords:** Fuel cell; Proton exchange membrane (PEM); Freeze; Cold start; State of water

### 1. Introduction

As the electric power generation apparatuses, proton exchange membrane (PEM) fuel cells have been in the limelight in vehicle applications. For PEM fuel cells being successfully used, one of the challenges is that they are able to be stored and operated at subzero temperatures [1]. Although debates about whether water freezing causes degradation of cell performance still exist [2,3], the fact that the self start of a PEM fuel cell is difficult at subfreezing temperatures has been generally accepted [4–6]. Since PEM fuel cells at subzero temperatures are subjected to the same polarizations as those at ambient temperature, the decrease of ohmic loss will be helpful for the PEM fuel cell cold start. As a result, the conductivity of the PEM at low temperatures might shed light on this concern.

The random copolymer Nafion<sup>®</sup> which consists of a polytetrafluoroethylene backbone and sulfonic acid groups attached on perfluorinated ether side chains [7] has been widely used as the PEM for fuel cells. Its proton transport mechanism mainly includes proton hopping (Grotthus mechanism) and vehicular diffusion [8,9]. The two modes of proton transport strongly depend on the water in the PEM. Although depression of the freezing point due to the confined space or strong acid environment occurs in Nafion<sup>®</sup> membrane, the freezing of water in the PEM will generally decrease the proton conductivity [10,11]. In addition, the state of water identified by differential scanning calorimetry (DSC) can be classified into freezable and nonfreezable water [12,13]. Therefore, the key issue is evidently that how the freezable or nonfreezable water accounts for the total water content and how they contribute to the conductivity.

In the development of high temperature fuel cells, there emerge various new alternative PEMs [14]. One series of them are nonperfluorinated materials based on engineering polymers which usually have a large degree of aromatic character.

\* Corresponding author. Tel.: +86 411 84379051; fax: +86 411 84379185.  
E-mail address: [hmyu@dicp.ac.cn](mailto:hmyu@dicp.ac.cn) (H. Yu).

Unfortunately, the conductivities of these PEMs at subzero temperatures are not extensively studied like that at the high temperatures. Subfreezing conductivities of several aromatic-based PEMs were screened in this paper. We aim to report the conductivities of PEMs which are favorable to the fuel cell cold start and to give some useful information on the further development of PEMs for subzero applications.

## 2. Experimental

### 2.1. Membranes

The sulfonated polyimide (SPI), sulfonated poly(ether ether ketone) (SPEEK) and disulfonated poly(arylene ether sulfone) copolymer (SPSU) used in this study were in-house synthesized and the detailed preparation methodology has been reported elsewhere [15–17]. The chemical structures are depicted in Fig. 1 as well as that of Nafion<sup>®</sup>. The different sulfonation degree of SPIs were achieved by varying the ratio of 4,4'-diamino-biphenyl 2,2'-disulphonic acid (BDSA) to 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA). All membranes were formed by casting solutions of the polymers onto glass plates. The as-cast membranes were soaked in 0.5 M sulfuric acid for more than 12 h to ensure full protonation. After that, the membranes were rinsed several times with deionized water.

### 2.2. Water uptake and conductivity

Water uptake was determined gravimetrically according to the typical method reported [16,17]. Membranes were soaked in deionized water or suspended in relative humidity (RH) 75% environment at 25 °C for more than 24 h. Following equilibration

the wet membranes were quickly weighed and measured. For the membranes soaked in water, the surface-attached water was quickly removed with a paper towel prior to measuring. The wet mass ( $m_{\text{wet}}$ ) and wet thickness ( $d_{\text{wet}}$ ) of the sample were thus determined. The membranes were vacuum-dried at 60 °C for 4 h and then measured again to obtain the dry mass ( $m_{\text{dry}}$ ) and the dry thickness ( $d_{\text{dry}}$ ). The water uptake and the swelling were calculated by following equations.

$$\text{water uptake} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \quad (1)$$

$$\text{swelling} = \frac{d_{\text{wet}} - d_{\text{dry}}}{d_{\text{dry}}} \times 100\% \quad (2)$$

The number of water molecules per sulfonic acid group ( $\lambda$ ) was determined from the ion-exchange capacity (IEC) and water uptake of membrane:

$$\lambda = \frac{m_{\text{wet}} - m_{\text{dry}}}{18m_{\text{dry}} \times \text{IEC}} \quad (3)$$

The membrane conductivity was measured by electrochemical impedance spectroscopy (EIS) using a PARSTAT<sup>®</sup> 2273A (Princeton, USA) electrochemical system. Signal amplitude of 20 mV in the frequency range of 1 MHz–100 Hz was applied. The sample was sealed between two electrodes with an area of 0.332 cm<sup>2</sup>, and then frozen down to –20 °C. The impedance measurement was then carried out. All the conductivity values reported here were recorded after the conductivity had reached a constant value for at least 1 h. When the impedance did not cross the real axis, the membrane resistance was obtained by extrapolating the impedance data to the real axis on the high frequency side [18]. The impedance data were all corrected for the contribution of the empty cell and the interfacial

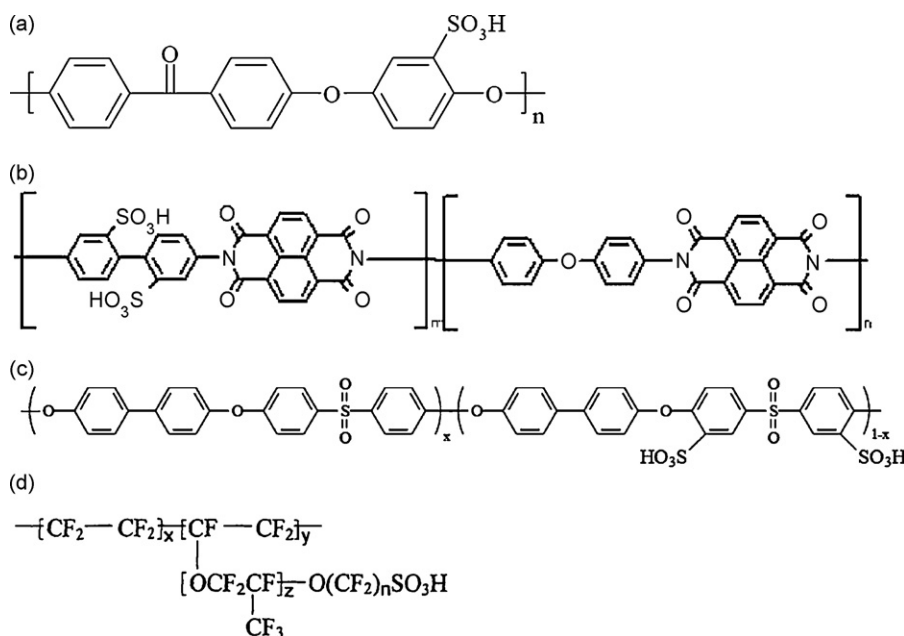


Fig. 1. Chemical structures of aromatic-based proton exchange membranes: (a) sulfonated poly(ether ether ketone) (SPEEK); (b) sulfonated polyimide (SPI); (c) disulfonated poly(arylene ether sulfone) copolymer (SPSU).

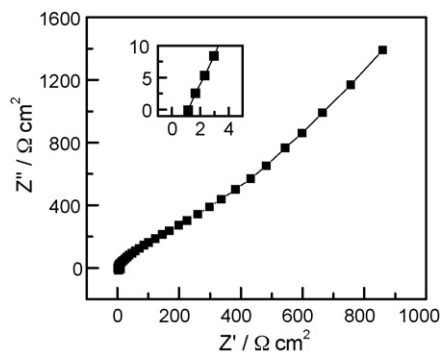


Fig. 2. Nyquist plot for Nafion<sup>®</sup> 212 membrane at  $-20\text{ }^{\circ}\text{C}$ .

resistance [18]. The conductivity values were calculated using Eq. (4).

$$\sigma = \frac{L}{RA} \quad (4)$$

where  $\sigma$  is the proton conductivity of the membrane,  $L$  is the membrane thickness,  $R$  is the membrane resistance, and  $A$  is the area of the electrode. A Nyquist plot for Nafion<sup>®</sup> 212 membrane at  $-20\text{ }^{\circ}\text{C}$  is shown in Fig. 2 and Nyquist plots for other membranes are similar in shape.

### 2.3. Differential scanning calorimetry

The DSC measurements were performed by a DSC141 (SETARAM Inc., France) system. Before the measurements, the water swollen membranes were wiped with tissue papers. Each sample was quickly weighted and sealed in an aluminum DSC pan. A typical run was made using 4–8 mg of the sample. The sample was cooled down to  $-50\text{ }^{\circ}\text{C}$ , and the melting thermogram was recorded in the temperature of  $-30\text{ }^{\circ}\text{C}$  to  $8\text{ }^{\circ}\text{C}$  at a constant heating rate of  $5\text{ K min}^{-1}$  under nitrogen atmosphere.

## 3. Results and discussion

The samples investigated are summarized in Table 1. The IEC value of each membrane is determined via titration, as described earlier [17]. The swelling in thickness for each membrane at the two hydrated states is also given in Table 1. During the conductivity measurement, it is difficult to obtain the actual thickness of the membrane at subzero temperatures. Thus, the conductivity data are determined based on the membrane thickness at  $25\text{ }^{\circ}\text{C}$ .

Fig. 3 presents the water uptake data and  $\lambda$  at  $25\text{ }^{\circ}\text{C}$  for different membranes in terms of IEC. Either immersed in water

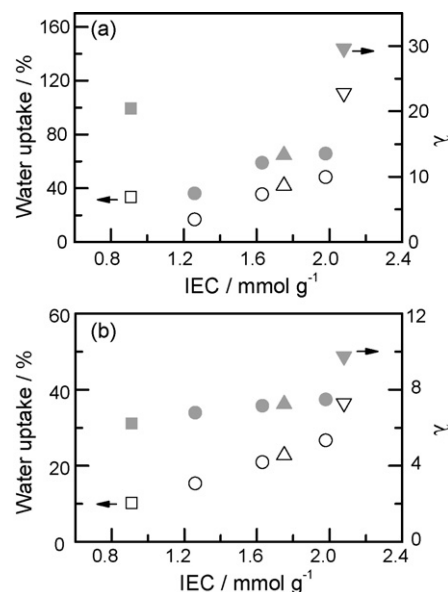


Fig. 3. Water uptake as a function of IEC values for sulfonated polymers of Nafion<sup>®</sup> 212 (□); SPIs (○); SPEEK (▽); SPSU (Δ) at  $25\text{ }^{\circ}\text{C}$ : (a) immersed in water; (b) humidified by water vapor at 0.75 activity.

(Fig. 3a) or humidified by water vapor at activity of 0.75 (Fig. 3b), the water content increases with the IEC value for the aromatic-based membranes. Although differences in molecular structure and bulk density exist among the membranes, the high IEC value of membrane yields a correspondingly high osmotic pressure and thus an increased water uptake [19]. An interesting phenomenon is that Nafion<sup>®</sup> 212 uptakes the smallest water content when the membranes are hydrated using water vapor at activity of 0.75 (Fig. 3b). According to successive steps in membrane hydration described by Zawodzinski [20], water first solvates the fixed ionic groups (water activity  $<0.75$ ) and counter-ions and then fills the hydrophilic zone of the membrane (water activity  $>0.75$ ). Nafion<sup>®</sup> has the smallest IEC value and therefore absorbs the lowest water content when it is humidified by water vapor at activity of 0.75. However, Nafion<sup>®</sup> 212 membrane with a relatively low IEC value absorbs comparable water content as SPI-2 when hydrated by liquid water. When the IEC is taken into account, fully hydrated Nafion<sup>®</sup> 212 membrane possesses a relatively high value of  $\lambda$  (Fig. 3a). This can be understood that more water is absorbed in hydrophilic phase for Nafion<sup>®</sup> 212 membrane.

Fig. 4 shows proton conductivities for the different membranes at fully hydrated states. For comparison, their conductivity data at  $25\text{ }^{\circ}\text{C}$  are also given. When the fully hydrated

Table 1  
Properties of membranes under two hydrated states at  $25\text{ }^{\circ}\text{C}$

Membrane	IEC (meq g <sup>-1</sup> )	Swelling in thickness (%) (in water)	Swelling in thickness (%) (in 0.75 vapor)
N212	0.91	20.0	5.2
SPI-1	1.26	20.8	8.1
SPI-2	1.63	25.6	9.2
SPI-3	1.98	40.3	12.4
SPEEK	1.75	13.8	6.9
SPSU	2.08	33.5	8.3

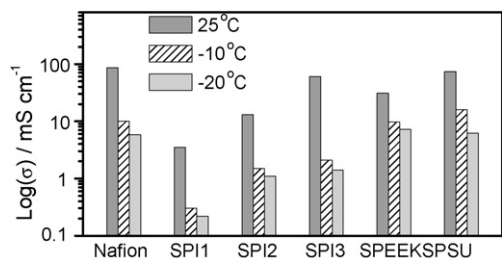


Fig. 4. Proton conductivity for different fully hydrated membranes.

Nafion® 212 membrane is frozen at  $-20^{\circ}\text{C}$  for about 2 h, its proton conductivity becomes  $5.8\text{ mS cm}^{-1}$ . Heating the cell to  $-10^{\circ}\text{C}$  enhances the conductivity to  $10\text{ mS cm}^{-1}$ . A further rise in temperature to  $25^{\circ}\text{C}$  causes the conductivity to reach the value of  $86.5\text{ mS cm}^{-1}$ , which is comparable with the value reported early [20]. From the ambient to subzero temperature, the conductivity for SPI series decreases more evidently. The conductivity at the three temperatures becomes larger with the increase of IEC value. However, for SPI-3 membrane, the conductivity reaches  $60\text{ mS cm}^{-1}$  at  $25^{\circ}\text{C}$  and falls to a smaller value at lower temperature. For the SPEEK and SPSU membranes, the conductivities at  $25^{\circ}\text{C}$  are  $31\text{ mS cm}^{-1}$  and  $73.4\text{ mS cm}^{-1}$ , respectively. This agrees well with the value reported in previous literature [17,21]. Their conductivities at lower temperatures are comparable with or even slightly higher than those of Nafion® membrane.

To prevent freeze degradation and benefit cold start at subzero temperatures, water in the fuel cell is usually removed by gas purge after the PEM fuel cell shut down operation [22,23]. Therefore, water vapor at 0.75 activity is utilized to humidify the PEMs and the conductivities are shown in Fig. 5. As expected, the conductivities fall in the region of  $1\text{--}20\text{ mS cm}^{-1}$  at ambient temperature due to the low water uptake in the membranes. The conductivities of these sulfonated aromatic-based membranes depend more strongly on the water content and Nafion® membrane with a relatively low value of IEC has a higher conductivity at ambient temperature. This is because the key difference exists between Nafion® membrane and aromatic-based membranes (Fig. 1): (i) backbone, the hydrophobic PTFE backbone of Nafion® is more flexible; (ii) hydrophilic and hydrophobic phases, the element fluorine makes more polar between Nafion® backbone and sulfonic acid group and thus induces more evident hydrophobic or hydrophilic phase; (iii) location of sulfonic acid group, the sulfonic acid

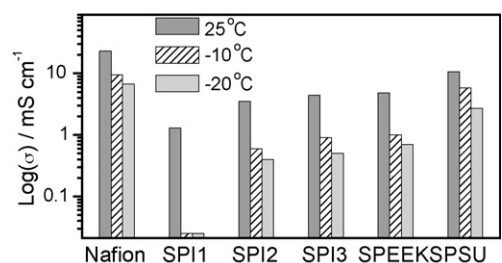


Fig. 5. Proton conductivity for membranes humidified by water vapor at activity of 0.75.

group is connected with the side chain of Nafion® forming fluorine–sulfonic acid while the sulfonic acid group is linked on the backbone of aromatic-based membranes forming weaker acidity of phenyl–sulfonic acid [19]. Besides, the conductivities of aromatic-based membranes except for SPSU membrane are almost smaller than  $1\text{ mS cm}^{-1}$  at subzero temperatures. Since the conductivity correlates with water amount in the PEM, it is necessary to investigate the water state at subzero temperatures.

The state of water in the PEMs intensively affects the proton transport properties. Bulk water will freeze at subzero temperature and the conductivity of the ice itself is very low (only  $10^{-5}\text{ mS cm}^{-1}$ ) [8]. The results in Fig. 4 indicate that the conductivities of the PEMs decrease but do not drop to zero at subzero temperatures. It is necessary to elucidate the contribution of different types of water in the PEMs to the conductivity via low temperature DSC. Typical melting thermograms determined by DSC are shown in Fig. 6. It can be seen that there are two peaks in the thermogram of fully hydrated SPSU membrane, which indicates the membrane contains at least two kinds of water. One of them, “free water”, behaves like bulk water and exhibits a sharp melting point at about  $0^{\circ}\text{C}$ . The other one, “freezable loosely bound water”, interacts weakly with the polymer chain [13]. Fully hydrated Nafion® membrane only shows a relatively broad thermogram which suggests the water is in more inhomogeneous environment. In any case, either free water or freezable loosely bound water can be treated as freezing water, which can be inspected from the DSC thermograms. The freezing water amount in the PEM can be expressed in terms of the freezing hydration number,  $\lambda_f$ , which is the number of freezing water molecules per sulfonic acid group. It can be estimated from the following equation.

$$\lambda_f = \frac{Q}{\Delta H v} \left( 1 + \frac{1}{n} \right) \lambda \tag{5}$$

where  $Q$  is the area under the peak thermogram,  $\Delta H$  is the heat of ice melting ( $334\text{ J g}^{-1}$ ),  $v$  is the DSC heating rate ( $5\text{ K min}^{-1}$ ),  $n$  is the water uptake in weight, and  $\lambda$  is the total hydration number. Usually, the freezing water amount calculated from Eq.

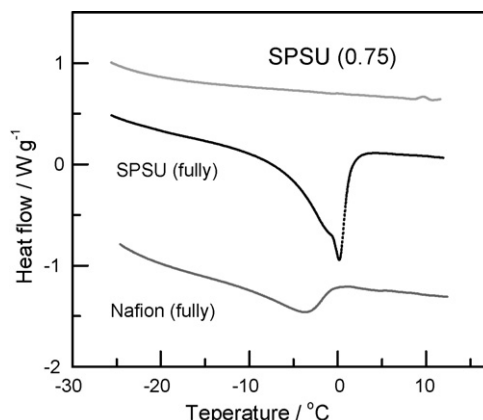


Fig. 6. Typical DSC melting thermograms.



(5) is smaller than the total water amount in the PEM. There is another state of water which cannot be detected by DSC. This kind of water can be termed as nonfreezing water. According to Ref. [12], the total water amount minus the freezing water amount achieves the nonfreezing water amount (Eq. (6)). Here, the nonfreezing hydration number,  $\lambda_{\text{nf}}$ , is used to express the nonfreezing water amount.

$$\lambda_{\text{nf}} = \lambda - \lambda_{\text{f}} \quad (6)$$

The nonfreezing water is strongly bound to the polymer chain and does not freeze at subzero temperatures. Table 2 summarizes the state of water in the PEMs. The nonfreezing hydration number varies from 12.8 to 17.8 for different fully hydrated PEMs. Furthermore, the amount of the freezing water in the fully hydrated SPEEK and SPI-3 is very little. The content of the freezing water in each PEM drops to zero when the water activity is decreased to 0.75.

Referring back to Figs. 4 and 5, the reason for that the proton conductivity reduces at lower temperatures at least includes: (i) transformation of freezing water to ice; (ii) temperature dependence of proton transport by nonfreezing water. The former can be easily understood. The latter can be explained as follows. After the PEM was humidified by water vapor at 0.75 activity, there is only nonfreezing water in it (Table 2). However, the conductivity of each membrane is still larger than  $1 \text{ mS cm}^{-1}$  which indicates the nonfreezing water also contributes to the proton transport. When the temperature decreases the conductivity decreases (Fig. 5) and this is due to the temperature dependence. Fully hydrated Nafion<sup>®</sup> membrane has higher nonfreezing water content than when it is humidified by water vapor (0.75 activity). It would be thought that the conductivity of fully hydrated membrane at  $-10^\circ\text{C}$  or  $-20^\circ\text{C}$  should be higher than when it is humidified by water vapor. The fact is not like that (as shown in Fig. 5). It is most likely that the formed ice in spherically shaped reverse micelles [7] shields the proton transport process through the nonfreezing water. For the SPI and SPEEK membranes, they contain very little freezing water, and thus ice shielding effect does not appear. Although there is high freezing water content in the fully hydrated SPSU membrane, its conductivity at  $-10^\circ\text{C}$  or  $-20^\circ\text{C}$  is higher than when it is humidified by water vapor. High conductivity at ambient temperature, low value of  $\lambda_{\text{f}}$  and unobvious dependence of conductivity on temperature will benefit subfreezing conductivity for an aromatic-based PEM.

Table 2  
State of water in the proton exchange membranes determined by DSC

Membrane	Fully hydrated (H <sub>2</sub> O/SO <sub>3</sub> H)		Humidified in water vapor (H <sub>2</sub> O/SO <sub>3</sub> H)	
	$\lambda_{\text{f}}$	$\lambda_{\text{nf}}$	$\lambda_{\text{f}}$	$\lambda_{\text{nf}}$
N212	5.3	15.2	0	6.2
SPI-3	0.7	12.8	0	7.5
SPEEK	0.4	12.9	0	7.2
SPSU	11.8	17.8	0	9.7

## 4. Conclusion

For the development of PEM fuel cell cold start at subzero temperatures, subfreezing conductivities of aromatic-based membranes and Nafion<sup>®</sup> 212 membrane were investigated. Although the aromatic-based PEMs at fully hydrated state had relatively high IEC values, their conductivities at ambient temperature were not higher than that of Nafion<sup>®</sup> membrane. The conductivity for all membranes leveled off with the temperature decrease. The fully hydrated SPEEK and SPSU membranes had comparable conductivities with Nafion<sup>®</sup> membrane at  $-10^\circ\text{C}$  or  $-20^\circ\text{C}$ . When water uptake in membranes was decreased, the subfreezing conductivities of the aromatic-based PEMs were all lower than that for Nafion<sup>®</sup> membrane. Combined with the analysis of the water state membranes measured via DSC, there were three impacts contributing to the reduced conductivity at subzero temperatures. They were freezing of the free water in the membrane, temperature dependence of proton transport through nonfreezing water and shielding effect of ice in the membrane on proton transport.

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