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Short communication

Conductivity of aromatic-based proton exchange membranes at subzero temperatures

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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® 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® 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.

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® 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® 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.

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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®. 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_{wet}) and wet thickness (d_{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_{dry}) and the dry thickness (d_{dry}). The water uptake and the swelling were calculated by following equations.

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

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

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

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

The membrane conductivity was measured by electrochemical impedance spectroscopy (EIS) using a PARSTAT® 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^2, 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

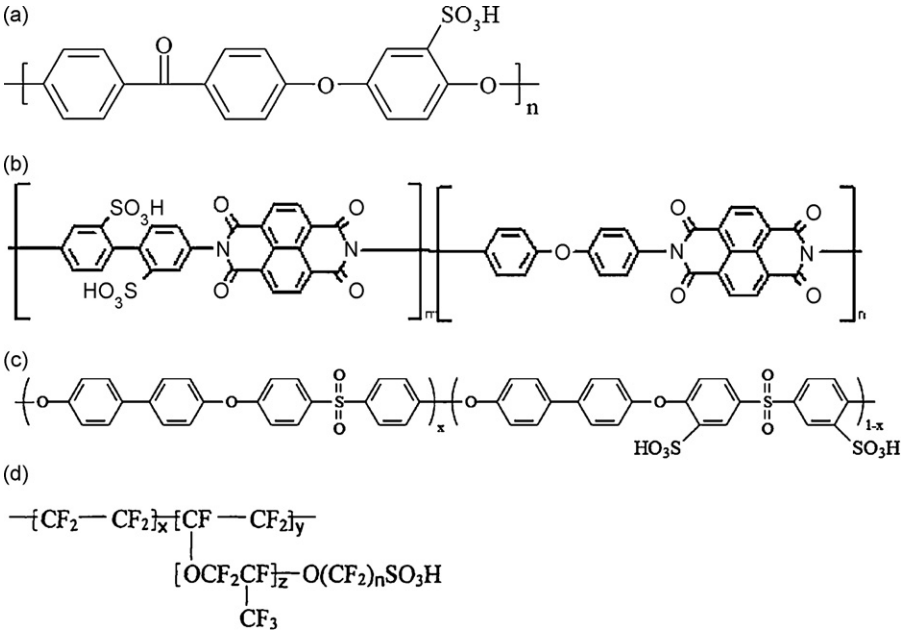

Fig. 1. Chemical structures of aromatic-based proton exchange membranes: (a) sulfonated poly(ether ether ketone) (SPEEK); (b) sulfonated polyimide (SPI); (c) disulfonated poly(arylene ether sulfone) copolymer (SPSU).