Short communication

Covalent-ionically cross-linked polyetheretherketone proton exchange membrane for direct methanol fuel cell

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ABSTRACT

In this paper, the proton exchange membrane prepared by covalent-ionically cross-linking water soluble sulfonated–sulfinated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (SsPEEK-WC) is reported. Compared with covalent cross-linked PEEK-WC membrane, this covalent-ionically cross-linked PEEK-WC membrane exhibits extremely reduced water uptake and methanol permeability, but just slightly sacrificed proton conductivity. The proton conductivity of the covalent-ionically cross-linked PEEK-WC membrane reaches to 2.1×10^{-2} S cm^{-1} at room temperature and 4.1×10^{-2} S cm^{-1} at 80 °C. The methanol permeability is 1.3×10^{-7} cm^2 s^{-1}, 10 times lower than that of Nafion® 117 membrane. The results suggest that the covalent-ionically cross-linked PEEK-WC membrane is a promising candidate for direct methanol fuel cell because of low methanol permeability and adequate proton conductivity.

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1. Introduction

Direct methanol fuel cell (DMFC) is attractive as a promising power source with several possible applications including automotive and portable power sources due to some of its advantages, such as high efficiency, low emissions, potentially renewable fuel source as well as fast and convenient refueling [1]. The proton exchange membrane is one of the key components of DMFC, which has double roles of conducting protons and separating the fuel from oxidant. DuPont's Nafion® is widely used as the proton exchange membrane in fuel cell, because of its high proton conductivity and excellent chemical stability [2]. However, the high cost limits the large-scale commercialization [3]. Another shortcoming of Nafion® is its high methanol permeability that drastically reduces the performance of DMFC [4]. Therefore, the membranes which have significantly reduced methanol permeability, lower price and high conductivity are required for the practical realization of DMFC. For those reasons, during the last decade, the preparation of low cost membranes based on non-fluorinated polymers as alternative to Nafion® has received much attention [5,6].

Poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) is cheap and chemically inert polymer. The sulfonated PEEK-WC (SPEEK-WC) membranes have been developed for possible fuel cell applications [7–10]. The membranes based on SPEEK-WC show good chemical stability, high proton conductivity, and both reduced methanol permeability and a lower cost as compared to Nafion® membrane. It was found that the proton conductivity and water uptake increase with increasing degree of sulfonation (DS). The proton conductivity of the non-cross-linked PEEK-WC membranes changes from 6×10^{-4} S cm^{-1} for DS = 0.1 to about 1×10^{-2} for DS = 1.04 at room temperature. However, the extremely high water uptake (up to 500% at 80 °C) which limits the mechanical stability, is not tolerable for fuel cell application [9].

The aim of the present work is to improve the proton conductivity of PEEK-WC based membrane with a reasonable water uptake for possible DMFC application. The novel proton exchange membrane was prepared by covalent and ionic cross-linking the sulfonated–sulfinated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (SsPEEK-WC) via simple route without using expensive materials. The properties of the cross-linked membrane, such as water uptake, proton conductivity, methanol permeability and thermal stability were investigated for fuel cell application.

2. Experimental

2.1. Chemicals

PEEK-WC was supplied by Changchun Institute of Applied Chemistry. Chlorosulfonic acid (97.0%), N-methyl-2-pyrrolidinone

(NMP), sodium hydroxide, and diiodomethane were purchased from Sigma–Aldrich. Polybenzimidazole (PBI) solution (10%) was kindly proved by Northeastern University. All chemicals were used without further purification.

2.2. Preparation of polymer

10 g of PEEK-WC was slowly added into 100 ml of concentrated chlorosulfonic acid under stirring for 10 h at room temperature. The mixture was precipitated in ice-water, and then washed with distilled water to neutral. Thereafter, the sulfonated–chlorosulfonated PEEK-WC (SCPEEK-WC) was dried in a vacuum oven at 70 °C. The sodium sulfite solution was added into the modified PEEK-WC as the reducing agent for 10 h at 80 °C and then washed with icy deionized water. The resulting sulfonated–sulfinated (SsPEEK) was dried in a vacuum oven. The ion exchange capacity (IEC) of SCPEEK-WC was determined by acid–base titration. The IEC was calculated by the following equations:

$$IEC \ (mmol \ g^{-1}) = \frac{Moles_{H^+}}{Mass_{polymer}} \cdot 1000 \tag{1}$$

Therefore, DS was calculated from IEC data by using Eq. (2) according to Basile et al. [7].

$$DS = \frac{IEC \times MW_{PEEK-WC}}{1000 - (IEC \times MW_{SO_3H})} \tag{2}$$

where MW is the molecular weight.

2.3. Preparation of membranes

Covalently cross-linked membrane: The cross-linker diiodomethane was added to the 15 wt% of SsPEEK-WC solution in NMP with magnetic stirring. The solution was cast on a glass Petri dish. Covalent-ionically cross-linked membrane: The diiodomethane for covalently cross-linking and polybenzimidazole solution for ionically cross-linking were added to the 15 wt% of SsPEEK-WC solution in NMP. After homogenization of the solution by stirring, the polymer solution was cast on a glass Petri dish.

In both cases, the solvent was removed in a vacuum oven at 130 °C. The membranes were peeled off from the Petri dish. Thereafter, the membranes were treated in 10 wt% of sodium hydroxide solution at 90 °C for 24 h, then in 10 wt% H$_2$SO$_4$ at 90 °C for 24 h and finally in water for 24 h at 90 °C. An uncross-linked membrane was also prepared, but was found to be water soluble.

2.4. Characterization of membranes

2.4.1. Water uptake

The water uptake of the cross-linked membranes was determined by measuring the weight difference between the fully hydrated membrane and the dry membrane. The following equation was used:

$$water \ uptake = \frac{G_w - G_d}{G_d} \times 100\% \tag{3}$$

where G_w is the weight of the wet membrane, and G_d is the weight of the dry membrane.

2.4.2. Proton conductivity measurement

A schematic representation of the cell for proton conductivity measurements is shown in Fig. 1. The fully hydrated membrane was sandwiched between two stainless steel electrodes with a contact area of 0.28 cm^2. The proton conductivity of the membrane was obtained from the impedance data. Impedance measurements were conducted using a potentiostat (Autolab PGSTAT30, Netherlands) in combination with the computer controlled frequency
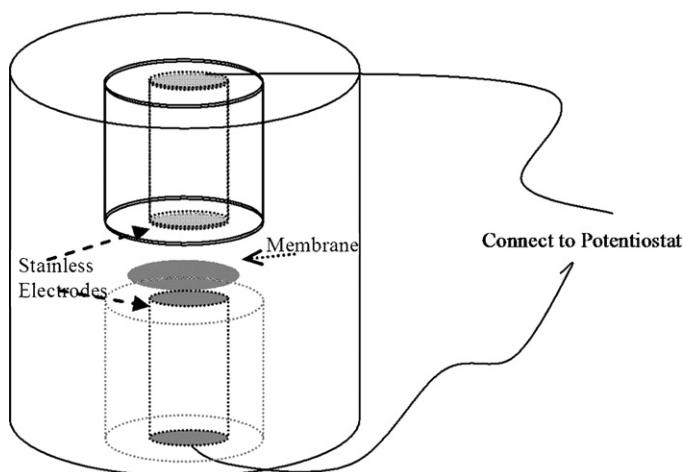

Fig. 1. Schematic representation of proton conductivity cell.

response analyzer over the frequency range from 0.1 Hz to 100 kHz. The proton conductivity σ was calculated, using the relationship:

$$\sigma = \frac{L}{RS} \tag{4}$$

where L, R and S are the thickness (cm), resistance (Ohm) and contact area of the membrane (cm^2), respectively.

2.4.3. Methanol permeability measurement

The methanol permeability was examined by using a diaphragm diffusion cell. The membrane was clamped in between two compartments. The methanol concentration changes with time were measured using gas chromatography (Hewlett Packard 5890) at 25 °C. The methanol permeability was calculated according to the following equation [11,12]:

$$P = \frac{L}{A} \times \frac{V_B}{C_A} \times \frac{\Delta C}{\Delta t} \tag{5}$$

where P is the methanol permeability, cm^2 s^{-1}; L is the membrane thickness, cm; A is the membrane area available for crossover, cm^2; V_B is the volume of the receiving compartment, cm^2; C_A is the initial concentration, M; Δt is measured time, s.

2.4.4. Thermogravimetric analysis

The thermal stability of membrane was analyzed in an argon atmosphere using a Thermal Analyzer STA 1500 (CCI-3, *Rheometric Scientific*) in a temperature range from 20 °C to 700 °C at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Water uptake

The water uptake of proton exchange membranes is related to mechanical strength and dimensional stability. These properties are very important for proton exchange membranes used in DMFC. Too much water will result in the excessive swelling of the membrane and further loss of its mechanical properties [13], thus rendering the membrane ineffective.

SCPEEK-WC was highly sulfonated (IEC = 1.87 mmol g, DS = 1.09), and was water soluble. In term of preparing PEEK-WC based membranes which are highly proton conductive and tolerable water uptake for possible fuel cell application, the SCPEEK-WC was converted to SsPEEK-WC by reducing sulfonyl chloride group to sulfinated group (Fig. 2). SsPEEK-WC has two types of functional groups, sulfonic group for proton exchange
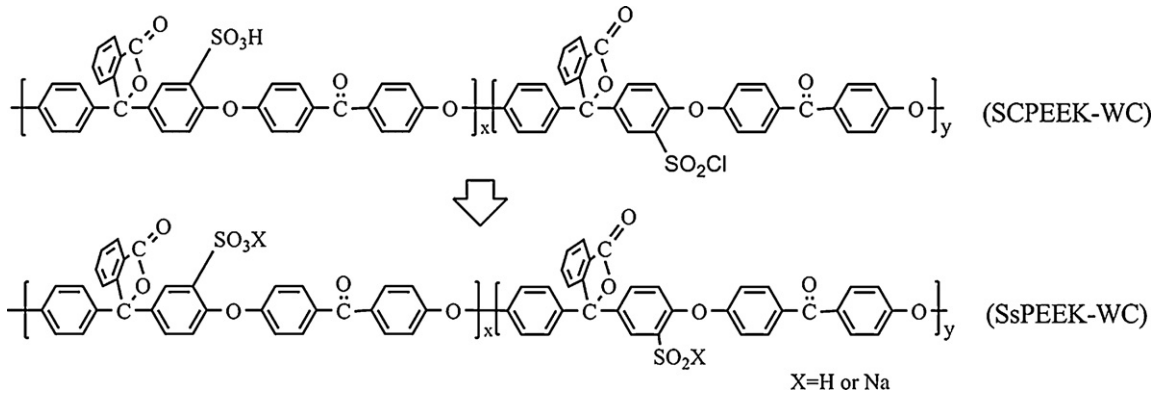
Fig. 2. SCPEEK-WC and SsPEEK-WC.

and the sulfinate group for covalent cross-linking. Without cross-linking, the prepared SCPEEK-WC and SsPEE-WC were all water soluble.

After cross-linking, the membranes became water insoluble. The water uptake of the covalently cross-linked PEEK-WC membrane was 44% at room temperature and reached 110% at 80 °C. Although, the value of water uptake at 80 °C was tolerable, however, to reduce the value of water uptake is indispensable for the membrane used in DMFC at higher temperature such at 80 °C. The covalent-ionically cross-linked PEEK-WC membrane exhibits a reduced increasing trend of water uptake with increasing temperature (Fig. 3). The water uptake was reduced to 43% at 80 °C. Decreasing water uptake is particularly important for membrane applications in DMFC as it will mean a longer lasting membrane without sagging.

3.2. Proton conductivity

The proton conductivities of the cross-linked membranes were determined from 20 °C to 80 °C. The membranes were fully hydrated during the measurement. Fig. 4 shows the proton conductivity of the cross-linked membranes as a function of temperature. It was found that the proton conductivity of the cross-linked membranes increases continuously with increasing temperature. The covalent-ionically cross-linked PEEK-WC membrane shows slightly reduced proton conductivity compared with that of covalently cross-linked PEEK-WC.
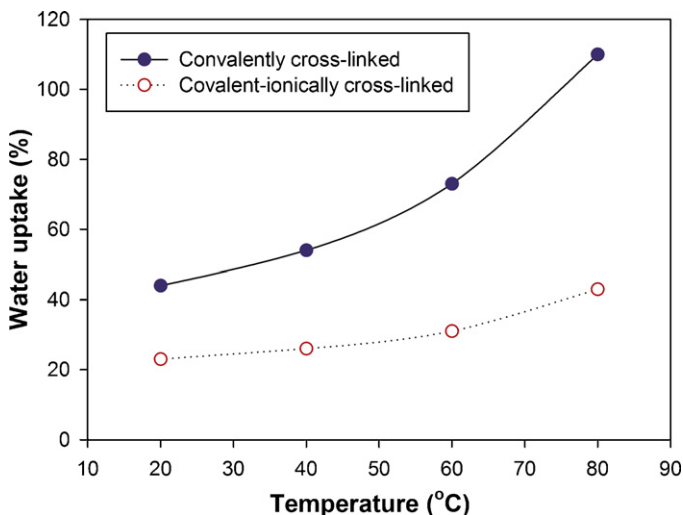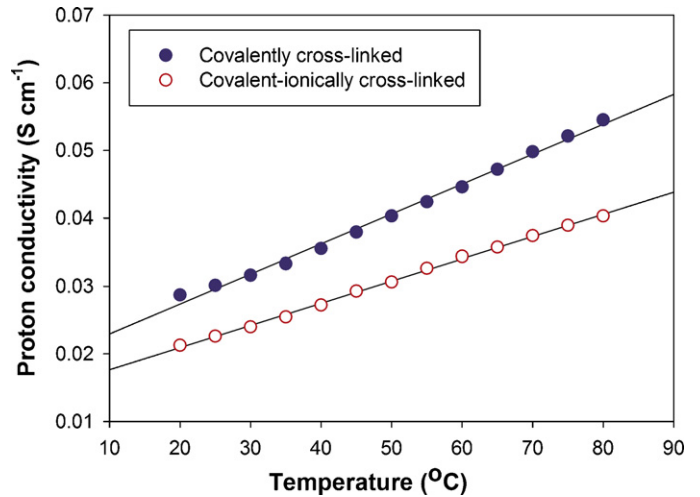

Fig. 4. Proton conductivity as a function of temperature.

The proposed network of the cross-linked membrane was formed via covalent bands and ionic bands as illustrated in Fig. 5. Those cross-linkages, the ionic bands between the main chain of PEEK-WC, the covalent bands between the main chain of PEEK-WC and main chain of PBI which form a three-dimensional network, and prevent the polymer from swelling to infinity, in other words from dissolving. This is due to the elastic retraction forces of
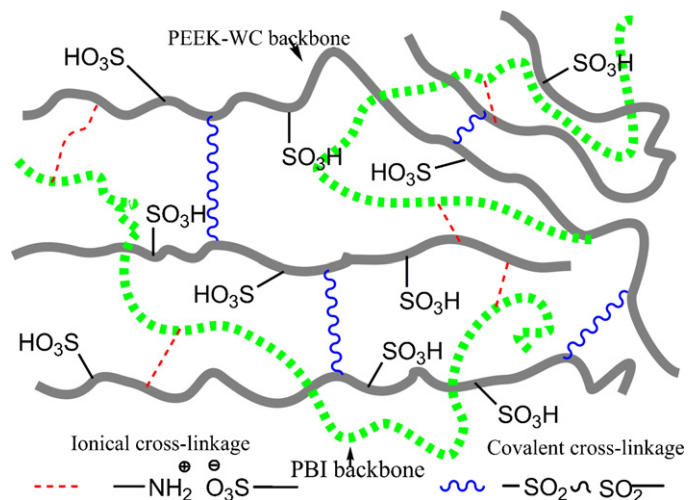

Fig. 3. Water uptake as a function of temperature.

Fig. 5. Network structure of covalent-ionically cross-linked membrane.

Table 1
The comparative properties of the cross-linked membranes.

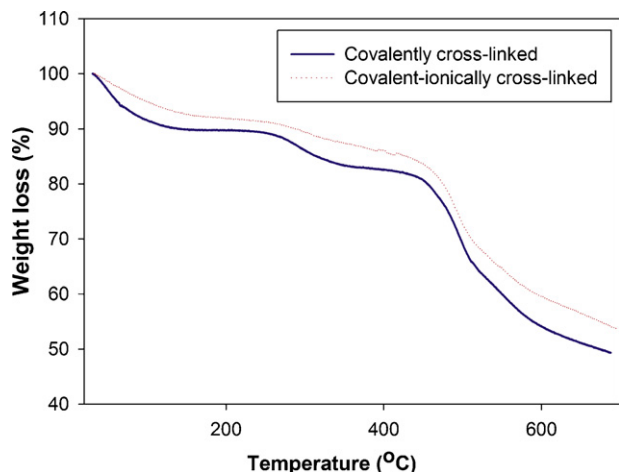| Membrane	Water uptake 20 °C (%)	Water uptake 80 °C (%)	Conductivity 20 °C (S cm^{-1})	Conductivity 80 °C (S cm^{-1})	Methanol permeability 20 °C (cm^2 s^{-1})
Covalently cross-linked	44	110	2.9×10^{-2}	5.5×10^{-2}	1.6×10^{-7}
Covalent-ionically cross-linked	23	43	2.1×10^{-2}	4.1×10^{-2}	1.3×10^{-7}
Nafion® 117	20	26	6.2×10^{-2}	9.7×10^{-2}	1.4×10^{-6}

Fig. 6. TGA of cross-linked PEEK-WC membranes.

the network which decreases the entropy of the chains as they become more dense after cross-linking [14]. The covalent-ionically cross-linked membrane shows reduced water uptake and slightly reduced proton conductivity compared with that of the covalently cross-linked membrane.

The proton conductivity of covalent-ionically cross-linked PEEK-WC membrane was 2.1×10^{-2} S cm^{-1} at 20 °C and reached to 4.1×10^{-2} S cm^{-1} at 80 °C. The proton conductivity of the cross-linked membrane is lower than that of Nafion® 117 (6.2×10^{-2} S cm^{-1} at 20 °C) which was measured at the same condition, however, the resistance of the cross-linked membrane can be reduced by reducing the thickness due to its extremely low methanol permeability.

3.3. Methanol permeability

It has been found that over 40 wt% of the methanol can be wasted in DMFCs across Nafion® membrane due to high methanol permeability [15]. In order to achieve improved high overall efficiency of DMFC, high permeability of methanol through the membrane has to be overcome [16].

It was found that the methanol permeability of the covalent-ionically cross-linked PEEK-WC membrane was reduced from 1.6×10^{-7} cm^2 s^{-1} to 1.3×10^{-7} cm^2 s^{-1} compared with that of covalent cross-linked PEEK-WC 1.6×10^{-7} cm^2 s^{-1}, much lower than that of Nafion® 117 membrane (1.4×10^{-6} cm^2 s^{-1}). The comparative properties of the prepared membranes are listed in Table 1.

3.4. Thermal stability

The thermal stability of membrane was analyzed by TGA. Three subsequent steps of weight loss are observed in Fig. 6. The absorbed water in the membrane causes the first weight loss from 20 to 150 °C. The second weight loss from 250 to 400 °C can be associated to the decomposing of the sulfonic groups from the main chain of PEEK [17,18]. The third weight loss is related to the decomposition of the main chain of PEEK from 400 °C. It was also observed that the covalent-ionically cross-linked membrane has got enhanced thermal stability comparing with that of covalently cross-linked membrane.

4. Conclusions

The covalent-ionically cross-linked PEEK-WC membrane shows reduced water uptake, reduced methanol permeability and enhanced thermal stability, but slightly reduced proton conductivity comparing with covalently cross-linked PEEK-WC membrane. The result suggested that the covalent-ionically cross-linked membrane is a promising candidate for DMFC application.

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