

PREPARATION AND PROPERTIES OF SPAES-TiO₂ HYBRID MEMBRANES FOR DIRECT METHANOL FUEL CELL*

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Abstract Sulfonated poly(arylene ether sulfone) (SPAES) copolymer with degree of sulfonation of 1.0 was synthesized and characterized. A series of SPAES-TiO₂ hybrid membranes with various contents of nano-sized TiO₂ particles were prepared and characterized through sol-gel reactions. Scanning electron microscopy (SEM) images indicated the TiO₂ particles were well dispersed within polymer matrix. These composite membranes were evaluated for proton exchange membranes (PEMs) in direct methanol fuel cell (DMFC). These membranes showed good thermal stability and mechanical properties. It was found that the water uptake of these membranes increased with the increase of the TiO₂ contents in the hybrid membranes. Meanwhile, the introduction of inorganic particles increased the proton conductivity and reduced the methanol permeability. The proton conductivities (0.118–0.162 S/cm) of SPAES-TiO₂ hybrid membranes with 8% TiO₂ particles are much higher than those of Nafion 117 membrane (0.095–0.117 S/cm) and pure SPAES membrane (0.100–0.124 S/cm) with degree of sulfonation of 1.0 at all temperatures (25–100°C). Especially, the methanol diffusion coefficient (8.4×10^{-7} cm²/s) of SPAES-TiO₂ hybrid membranes with 8% TiO₂ is much lower than that of Nafion 117 membrane (2.1×10^{-6} cm²/s). SPAES-TiO₂ hybrid membranes were therefore proposed as candidates of material for PEM in DMFC.

Keywords: SPAES; TiO₂; PEM; DMFC.

INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) have been identified as environmentally attractive energy sources for application both in stationary power and automobiles because of their low emissions and high conversion efficiency^[1, 2]. As one of the most important components of PEMFC, proton exchange membrane (PEM) transfers protons from anode to cathode as well as providing a barrier to fuel gas cross-leaks between the electrodes^[3]. Currently, the most commonly used membrane materials are perfluorinated polymers such as Dupont Nafion. Although, they exhibit good mechanical properties and long-time stability, their high cost and loss of proton conductivity at temperatures above 80°C as well as high methanol permeability have limited their widespread commercial application in PEMFC and DMFC^[4–7]. Therefore, numerous efforts have been dedicated to develop new PEM materials.

An applicable PEM in DMFC should possess high proton conductivity, low methanol permeability and adequate mechanical strength, *etc.*^[8]. Now the main obstacle for the development of DMFC is high methanol permeability. In last years, organic-inorganic nano composites offered exceptional opportunities to improve some properties of the membranes without sacrificing other important properties of PEM^[9–12]. For example, the organic-inorganic nanocomposite membrane has become an important approach to decrease methanol permeability^[13, 14].

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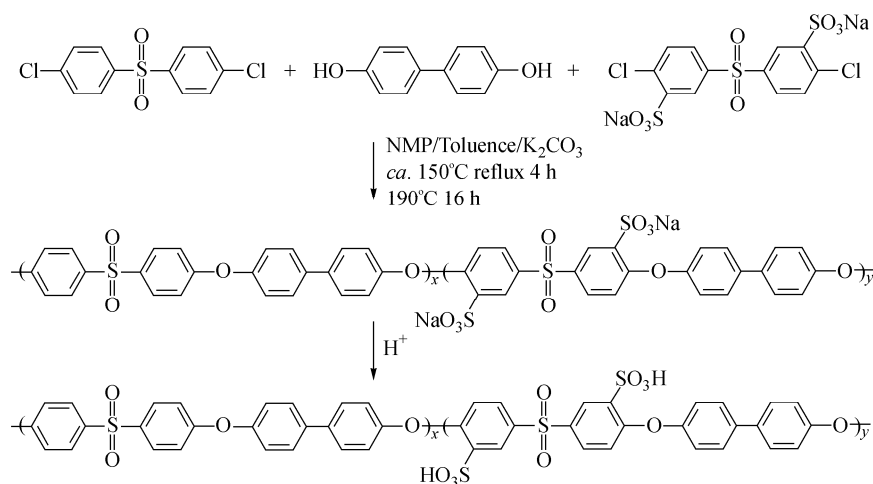
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Sulfonated poly(arylene ether sulfone) (SPAES) is a novel environment-friendly material and a high-performance engineering thermoplastics with excellent mechanical property, high thermal stability and has been examined systematically as an alternative PEM material^[15–17]. However, the methanol permeability of SPAES with high sulfonated degree is not low enough for PEM in DMFC. Therefore, attempts are being made to reduce the methanol permeability by doping with inorganic nano-sized particles. In this paper, SPAES is used as the matrix of polymer with a high degree of sulfonation ($D_s = 1.0$). A series of SPAES-TiO₂ hybrid membranes with various contents of nano-sized TiO₂ particles were prepared through sol-gel reactions. The influence of the content of TiO₂ nanoparticles on the properties of composite membranes was investigated and evaluated for DMFC.

EXPERIMENTAL

Polymer Synthesis and Characterization

The degree of sulfonation (D_s), which is the number of sodium sulfonate groups per repeating unit, was controlled by adjusting the amount of sulfonated monomer added. In this study, SPAES is used as the matrix polymer and is synthesized with calculated D_s value of 1.0. As shown in Scheme 1, SPAES polymer was synthesized *via* direct aromatic nucleophilic substitution condensation of 4,4'-bisphenol (BP, 7.448 g), 4,4'-dichlorodiphenylsulfone (DCDPS, 5.744 g) and disodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS, 9.724 g) in a NMP/toluene solvent system. The reaction mixture was heated under reflux at about 160°C for 4 h to dehydrate the system. Next, the temperature was raised to 190°C and kept at this temperature until the solution became very viscous. The reaction product was cooled to room temperature, added into deionized water to remove residual salts, and dried under vacuum at 120°C for 24 h. The yield of SPAES was about 90%. The number-average molecular weight of the obtained sample is 41600, the weight-average molecular weight of it is 53400, and the polydispersity index is 1.28. The degree of sulfonation ($D_s = 0.96$) of the polymer measured by titration is consistent with the calculated value ($D_s = 1.0$), which clearly suggests that D_s can be readily manipulated by controlling the amount of sulfonated monomer added.



Scheme 1 Synthesis of sulfonated poly(arylene ether sulfone)

The successful introduction of sodium sulfonate groups of SPAES was confirmed by FT-IR spectrum (Fig. 1) and ¹H-NMR spectrum (Fig. 2). The absorption bands at 1027 and 1095 cm⁻¹ can be assigned to the asymmetric and symmetric stretching vibrations of the sodium sulfonate groups in Fig. 1. ¹H-NMR (400 MHz, DMSO, δ): 7.01 (H_e), 7.11–7.21 (H_{a, c, h}), 7.70–7.75 (H_{d, i}), 7.84 (H_f), 7.94 (H_b), 8.30 (H_g).

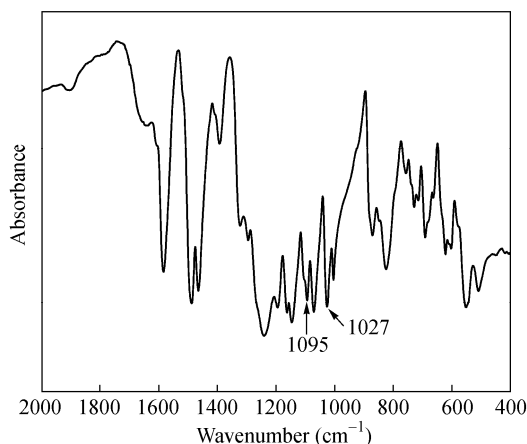
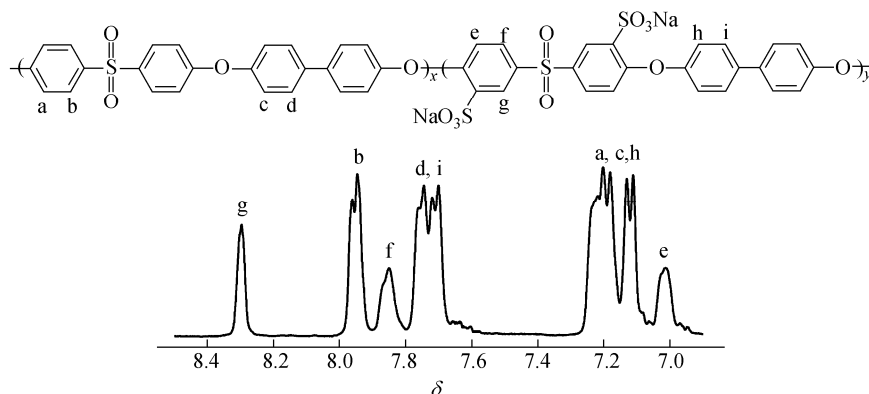


Fig. 1 FT-IR spectra of SPAES

Fig. 2 ¹H-NMR of SPAES

Preparation of Organic-Inorganic Composite Membranes

First, 10% SPAES solutions were made by adding certain amount of SPAES into DMAc. Then, Ti[OBu]₄, HCl, H₂O, and DMAc were mixed together in a ratio of 10:0.2:2:10 and stirred thoroughly into a homogeneous solution. A series of hybrid membranes with different TiO₂ contents (2%, 4%, 6%, 8% ...) were prepared by adding various amounts of Ti-containing sols into the SPAES solutions, followed by vigorous stirring and lasted at least 24 h. The mixed solutions were cast onto glass plates and dried at 50°C for 24 h. The membranes were further dried at 100°C for 12 h in order to facilitate the formation of TiO₂ matrix^[12].

The composite membranes with TiO₂ contents more than 8% became so easy to crack and could not meet the requirement of PEM. Therefore, SPAES-TiO₂ hybrid membranes with TiO₂ contents from 2% to 8% were investigated as follows.

Characterization

FT-IR and ¹H-NMR

FT-IR spectra of the membranes were recorded on a spectrum One B FT-IR spectrometer (Perkin-Elmer Co., USA). ¹H-NMR spectra were performed on an av 400 ¹H-NMR spectrometer (Bruker Co., Switzerland) using DMSO-d₆ as solvent and tetramethylsilane (TMS) as internal standard.

GPC (gel permeation chromatography)

GPC analysis was carried out on a Waters 410 chromatograph (Waters Co., USA) equipped with a Waters Wato44219 HT6E gel column and a refractive index detector. Tetrahydrofuran (THF) was applied as eluant at a flow rate of 1.0 mL/min at 60°C. Calibration was made by polystyrene (PS) as the standard.

Thermogravimetric analysis (TGA)

Dynamic TGA was employed to show the thermal stability (weight loss) of the copolymers with a ZRY-2P thermogravimetric analyzer (Shanghai Precision Scientific Instrument Co., Ltd., China). All the samples were first vacuum-dried and kept in the TGA furnace at 150°C for 30 min to remove water, and then cooled to room temperature. The heating rate was 10 K/min.

Membrane morphology

The membrane morphology was investigated by field emission scanning electron microscopy with an MX2600 FE (Camsan Co., Britain) equipment with electron beam energy of 20 kV. The composite membranes were vacuum sputtered with a thin layer of Au/Pd prior to examination.

Water uptake (WU) of membranes

The water uptake of the membranes was determined gravimetrically. The membranes were vacuum-dried at 100°C for 24 h, weighed and then immersed in deionized water at room temperature for 48 h. The wet membranes were wiped dry and quickly weighed again. The water uptake of the membranes was calculated according to Eq. (1).

$$WU = (M_{\text{wet}} - M_{\text{dry}}) / M_{\text{dry}} \times 100\% \quad (1)$$

Where, M_{wet} and M_{dry} refer to the weight of the wet membrane and the weight of the dry membrane, respectively.

Ion exchange capacity (IEC)

Titration was used to quantitatively determine sulfonic acid concentration in the copolymer. First, the protonic form membranes were converted to the sodium ionic form membranes by immersing the membranes in 2 mol/L NaCl solution for 48 h to exchange the H^+ ions with Na^+ ions. Then, the solutions were titrated with a 0.1 mol/L NaOH solution. IEC (meq/g) was calculated by Eq. (2):

$$IEC = (c \times V) / M_{\text{dry}} \times 1000 \quad (2)$$

Where c is the concentration of NaOH solution, V is the volume of NaOH solution and M_{dry} is the weight of the dried membranes.

Proton conductivity of membranes

The impedance of each acidified film was performed in a frequency range of 10 mHz to 0.1 MHz under fully hydrated conditions using an electrochemistry synthesis analyzer Potentiostat/Galvanostat Model 263A (Perkin-Elmer Co., USA). The resistance of the film was recorded when the imaginary resistance was at a minimum. The detailed procedure has been reported previously^[15].

The proton conductivity was calculated by Eq. (3).

$$\sigma = L / RS \quad (3)$$

Where σ is the proton conductivity (S/cm), L is the length between electrodes (cm), R is the membrane resistance (Ω) and S is the cross-sectional area of the film (cm^2).

Methanol diffusion coefficient

Diffusion coefficients were determined by using the cell mentioned in the literature^[18]. Methanol was placed on one side of the cell and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. Methanol analysis was performed by using a SHTMADU GC-4890 chromatograph (Shimadzu Co., Japan). Peak areas were converted to methanol concentration by using a calibration curve. The methanol diffusion coefficient was calculated and obtained according to the Eq. (4).

$$c_{B(t)} = \frac{A}{V_B} \frac{D_K}{L} c_A (t - t_0) \quad (4)$$

Where, c_B and c_A are the methanol concentration of permeated and feed side through the membrane,

respectively. A , L and V_B are the effective area of membrane, the thickness of membrane and the volume of permeated compartment, respectively. $(t-t_0)$ is the time during the whole penetration. D_K is the methanol diffusion coefficient.

Mechanical properties

Mechanical tensile tests were performed using an INSTRON 1121 Universal Testing Machine (INSTRON Co., USA) at room temperature with a crosshead displacement speed of 2 mm/min. For each testing reported, at least three specimens were taken, and average value was calculated.

RESULTS AND DISCUSSION

Microstructure of the Hybrid Membrane

SEM images of SPAES-TiO₂ composite membranes with different TiO₂ contents are shown in Fig. 3. It can be seen that the additive cluster size increased with the increase of the contents of inorganic composite. The particle diameters of the composite membrane containing 2% TiO₂ were in the range from 10 nm to 25 nm; the particle diameters of the composite membrane containing 4% TiO₂ were in the range from 20 nm to 50 nm; when the content of TiO₂ increased to 6% and 8%, the particle diameters of the composite membrane were about in the range from 30 nm to 80 nm, and some aggregation could be found. All the SEM images also suggested that TiO₂ particles dispersed into the membranes were nano-sized.

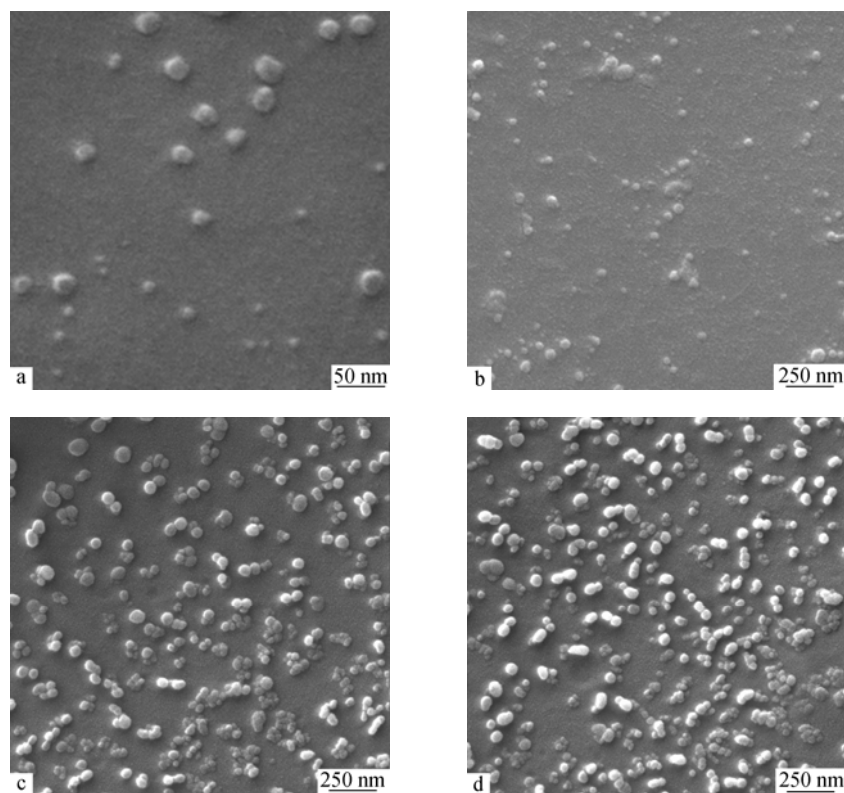


Fig. 3 SEM pictures of (a) 2% TiO₂, (b) 4% TiO₂, (c) 6% TiO₂ and (d) 8% TiO₂

Thermal Stability

The TGA curves of SPAES-TiO₂ composite membranes with different TiO₂ contents are given in Fig. 4. The copolymers were all stable at about 260°C, which represented the good thermal stability of copolymers. Two weight loss steps are observed in Fig. 4. The first weight loss step was about from 270°C to 400°C, which was

assigned to the loss of sulfonic acid groups of SPAES. The second weight loss step was at 400°C, which corresponds to the decomposition of main polymer chains. The 5% and 10% weight loss temperatures of SPAES with different contents of TiO₂ from 0% to 8% are about in the ranges of 309°C to 326°C and 352°C to 371°C, respectively (Table 1). The decomposition temperatures of all hybrid membranes are high and the introduction of nanosized TiO₂ particles can not influence the thermal stability of the membranes dramatically. From these results, it is concluded that the SPAES-TiO₂ composite membranes are thermally stable within the temperature range for PEMFC applications.

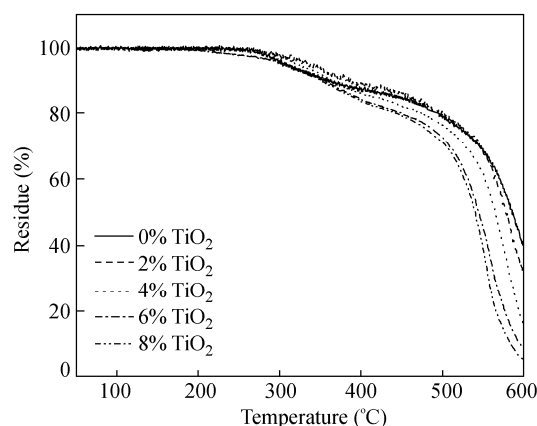


Fig. 4 The TG curves of SPAES/TiO₂ composite membranes

Table 1. The analytic data of SPAES membranes

Properties	TiO ₂ -0%	TiO ₂ -2%	TiO ₂ -4%	TiO ₂ -6%	TiO ₂ -8%	Nafion 117
T_5 (°C)	311	326	321	310	309	–
T_{10} (°C)	360	371	365	359	352	–
WU (%)	58	64	68	73	79	38
IEC _m (meq/g)	1.97	1.95	1.92	1.89	1.86	0.91
Conductivity (S/cm) at 25°C	0.100	0.105	0.109	0.112	0.118	0.096
Conductivity (S/cm) at 80°C	0.120	0.129	0.137	0.146	0.154	0.114

Ion Exchange Capacity (IEC) and Water Uptake of Membranes

Both IEC and water uptake play very important role in PEM. From the IEC results listed in Table 1, it can be seen that the IEC values of hybrid membranes are close to that of pure SPAES. Therefore, the water uptake of the membranes will be the most key factor influencing the proton conductivity of the membranes. Table 1 lists the water uptake of the hybrid membranes at room temperature. It can be seen that the water uptake increases with the increase of the contents of nano-sized TiO₂ particles due to the strong hydrophilicity of TiO₂ particles on their surface. Therefore, the nano-sized TiO₂ particles induced the higher water uptake of hybrid membranes than that of the pure SPAES membrane. That is also the reason why the proton conductivities of SPAES-TiO₂ membranes increase with the increase of water uptake (Fig. 5).

Proton Conductivity

The proton conductivities of the membranes with different contents of nano-sized TiO₂ particles were estimated by AC impedance spectroscopy. The conductivity data are listed in Table 1 and plotted in Fig. 5 as a function of temperature. From an application point-of-view, good proton conductivity is clearly one of the most important properties of PEM. Figure 5 showed that the introduction of inorganic particles increased the proton conductivities of the membranes under the same temperature condition. Moreover, the proton conductivities of SPAES-TiO₂ hybrid membranes increased with the increase of nano-sized TiO₂ particles because of the strength of hydrophilicity of TiO₂ particles. All the membranes showed higher proton conductivities than that of Nafion

117 membranes at all temperatures (25–100°C). Especially, the proton conductivities (0.118–0.162 S/cm) of the hybrid membranes with 8% TiO₂ particles are much higher than that of Nafion 117 membrane (0.095–0.117 S/cm) and pure SPAES membrane (0.100–0.124 S/cm) at all temperatures. Moreover, similar to Nafion 117 membrane, the proton conductivities of all the membranes increased with the increase of temperature. It is also noted that the proton conductivities of these membranes showed more marked increment with the increase of temperature than that of Nafion 117 membrane.

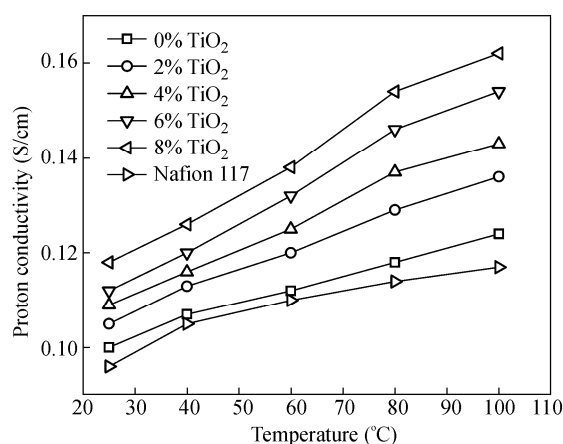


Fig. 5 Proton conductivity of membranes with different temperature

Methanol Diffusion Coefficient

One of the major drawbacks of the commercial Nafion membranes used as PEMs in DMFC systems is their high methanol permeability. Methanol diffusion coefficient of SPAES-TiO₂ composite membranes were shown in Fig. 6. It is easy to find that the methanol diffusion coefficient of these composite membranes decreased with the increase of the contents of TiO₂ particles. The reason is that the addition of TiO₂ particles filled the transport channels, reduced the size of the diameter of the channels and impeded the methanol molecules permeability. Especially, when the contents of TiO₂ particles increased to 4%, 6% and 8%, the methanol diffusion coefficient of the composite membranes (1.6×10^{-6} – 8.4×10^{-7} cm²/s) was lower than that of pure SPAES membrane (2.7×10^{-6} cm²/s) and Nafion 117 membrane (2.1×10^{-6} cm²/s). Thus, the results showed that the methanol permeability of the SPAES-TiO₂ composite membranes was effectively reduced comparing with pure SPAES membrane. Therefore, the SPAES-TiO₂ composite membranes may be candidates of PEM material in DMFC.

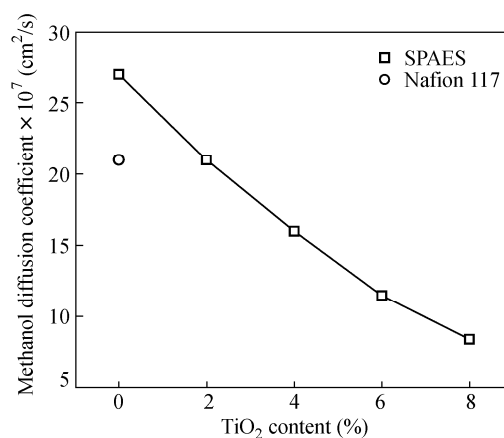


Fig. 6 Methanol diffusion coefficient of SPAES/TiO₂ composite membrane

Mechanical Properties

It is essential for PEMs to possess adequate mechanical strength to withstand fabrication of the membrane electrode assembly and operation in fuel cell. Here, the mechanical properties of SPAES-TiO₂ composite membranes are shown in Table 2. All the membranes show tensile strength in the range from 35.92 MPa to 30.18 MPa, which are higher than that of Nafion 117 membrane and are enough for the usage of PEM. And the tensile modulus for all the SPAES-TiO₂ composite membranes (1.09–1.85 GPa) are much higher than that of Nafion 117 membrane (0.26 GPa). One primary use of fuel cell is dynamical device of vehicle, so the accessories in fuel cell must have high aseismatic property. The membranes with high modulus can be highly airproof and not easy to be distorted at high temperature under the operating condition of fuel cell when being used as PEM. Thus, the SPAES-TiO₂ composite membranes prepared in this study can adequately meet the requirement of fuel cell.

Table 2. The mechanical properties of SPAES/TiO₂ composite membranes

Polymer	Tensile strength (MPa)	Tensile modulus (GPa)	Maximum elongation (%)
TiO ₂ -0%	35.92	1.85	3.28
TiO ₂ -2%	40.46	1.88	3.21
TiO ₂ -4%	34.28	1.62	2.80
TiO ₂ -6%	31.65	1.31	2.16
TiO ₂ -8%	30.18	1.09	2.02
Nafion 117	25.65	0.26	197.71

CONCLUSIONS

A series of SPAES-TiO₂ hybrid membranes with different contents of TiO₂ were prepared by sol-gel process. The composite membranes exhibited good thermal stability and mechanical properties. The introduction of TiO₂ particles into the membranes increased the water uptake and proton conductivity, moreover it caused the higher proton conductivity at higher temperatures. The methanol diffusion coefficient of the composite membranes decreased with the increase of the contents of TiO₂. Especially the methanol diffusion coefficient of membrane with 8% TiO₂ content is 8.4×10^{-7} cm²/s, which is much lower than that of Nafion 117 membrane. As a result, SPAES-TiO₂ composite membranes may be good alternative materials for PEM in DMFC.

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