



Sulfonated titania submicrospheres-doped sulfonated poly(ether ether ketone) hybrid membranes with enhanced proton conductivity and reduced methanol permeability

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ABSTRACT

Sulfonated titania submicrospheres (TiO₂-SO₃H) prepared through a facile chelation method are incorporated into sulfonated poly(ether ether ketone) (SPEEK) to fabricate organic-inorganic hybrid membranes with enhanced proton conductivity and reduced methanol permeability for potential use in direct methanol fuel cells (DMFCs). The pristine titania submicrospheres (TiO₂) with a uniform particle size are synthesized through a modified sol-gel method and sulfonated using 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt as the sulfonation reagent. The sulfonation process is confirmed by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectra (XPS). The hybrid membranes are systematically characterized in terms of thermal property, mechanical property, ionic exchange capacity (IEC), swelling behavior, and microstructural features. The methanol barrier property and the proton conductivity of the SPEEK/TiO₂-SO₃H hybrid membranes are evaluated. The presence of the fillers reduces methanol crossover through the membrane. Compared with the unsulfonated TiO₂-doped membranes, the TiO₂-SO₃H-doped ones exhibit higher proton conductivity due to the additional sulfonic acid groups on the surface of TiO₂. The hybrid membrane doped with 15 wt.% TiO₂-SO₃H submicrospheres exhibits an acceptable proton conductivity of 0.053 S cm⁻¹ and a reduced methanol permeability of 4.19 × 10⁻⁷ cm² s⁻¹.

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1. Introduction

In recent years, the oil crisis and the environmental deterioration have aroused increasing concern for the development of more efficient and cleaner energy technologies. Direct methanol fuel cells (DMFCs) with advantages of high power density and environmental friendliness are regarded as one of the most promising candidates. However, the development of DMFCs has been seriously hampered by the lack of efficient proton exchange membranes (PEMs) with both high proton conductivity and alcohol barrier property. The current state-of-the-art proton exchange membranes are made of perfluorosulfonic polymers featured by Nafion[®] (Dupont) which is well known for its high proton conductivity and good chemical stability. However, the high cost and the poor methanol-rejecting performance of Nafion[®] membranes limit its widespread application in DMFCs. Synthesizing novel PEMs with reasonable

conductivity, higher resistance to methanol and lower cost is one of the key tasks for the development of DMFCs [1–4].

Poly(ether ether ketone) (PEEK) is a hydrocarbon-based polymer possessing relatively high chemical stability, low methanol permeability, low cost, and reasonable proton conductivity after sulfonation. Sulfonated PEEK (SPEEK) has been extensively studied as an alternative membrane material for DMFCs [5–8]. However, while the high degree of sulfonation endows the membrane with high proton conductivity, the high sulfonation degree causes severe swelling and reduction in mechanical strength, thus leading to an undesirable methanol crossover. A number of approaches have been conducted to overcome this negative impact, including blending the acidic SPEEK with basic polymers [5], covalent crosslinking [6] and addition of inorganic fillers [7,8].

Among the various strategies explored, the organic-inorganic hybrid route (via sol-gel process or physical blending) has attracted much attention due to the extraordinary properties combining the characters of the organic moiety (e.g., flexibility and ductility) and the inorganic moiety (e.g., rigidity and thermal stability) [7–12]. It has been reported that doping of ceramic particles including montmorillonite [7], titanium oxide [8], zeolite [9], silica [10] and zirconium oxide [11] into polymer matrix could improve the

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methanol resistance and strengthen the mechanical and thermal stability of the hybrid membranes. However, in many cases, proton conductivity decreases with the addition of the inorganic fillers due to the rather low proton conductivity of the fillers themselves and their considerable dilution effect on the proton-exchange groups in the original polymer matrix [2,10]. The surface modification of the fillers via stable acid functionalization is proved to be an effective way to compensate, to some extent, the loss of proton conductivity caused by addition of the inorganic fillers. Nunes and coworkers blended sulfonated montmorillonite into SPEEK and obtained a proton conductivity 4-fold higher than the pristine one [7]. Liu et al. utilized sulfonated silica nanoparticles as fillers to modify the sulfonated poly(arylene ether ether ketone) and polybenzimidazole. It was found that both the two nanocomposite membranes exhibited enhanced proton conductivity and depressed methanol permeability [10,13]. In our previous study, zeolites with sulfonic acid groups on the surface were doped into chitosan to improve the proton conductivity and the organic–inorganic interface compatibility [14]. The modification processes of these ceramic oxides usually involved silane coupling agents, and required several time-consuming steps under specific conditions.

The complexation concept provides a facile approach for modification of metal oxide surface. It is well-known that catechol and catecholic derivatives could readily chelate with Ti ions to form a stable Ti–catecholic salt chelate complex at ambient temperatures [15–18]. In our previous work, organophosphorylated titania (OPTi) submicrospheres were prepared and incorporated into chitosan matrix, and the effect of surface acidification with mediate strong acid groups ($-\text{PO}_3\text{H}_2$) was investigated [19]. Herein, we described a novel and facile approach to synthesize sulfonated titania ($\text{TiO}_2\text{-SO}_3\text{H}$) submicrospheres by a similar chelation approach using 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt (Tiron) as the sulfonation reagent. The effect of surface acidification with strong acid groups ($-\text{SO}_3\text{H}$) was studied. The resulted $\text{TiO}_2\text{-SO}_3\text{H}$ submicrospheres were doped into SPEEK matrix to fabricate SPEEK/ $\text{TiO}_2\text{-SO}_3\text{H}$ hybrid membranes. The as-synthesized $\text{TiO}_2\text{-SO}_3\text{H}$ particles and the hybrid membranes were characterized by TEM, FTIR, XPS, SEM and TGA. The effects of $\text{TiO}_2\text{-SO}_3\text{H}$ incorporation on membrane properties, including membrane morphology, swelling behavior, thermal stability, mechanical strength, methanol permeability and proton conductivity were investigated.

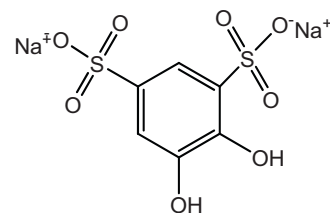
2. Experimental

2.1. Materials and chemicals

Poly(ether ether ketone) Victrex 381 G was purchased from Victrex High-performance Materials (Shanghai, China) Co., Ltd. 4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt (Tiron, 99%) was purchased from Xiya Chemical Co., Ltd. (Chengdu, China). Tetrabutyl titanate (TBT >98 wt.%) and ethylene glycol were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). N,N-dimethyl formamide (DMF), sulfuric acid, acetone, and methanol were of analytical grade and purchased locally. De-ionized water was used throughout the study.

2.2. Preparation of sulfonated poly(ether ether ketone)

PEEK was dried at 80 °C for 24 h followed by dissolving in concentrated sulfuric acid (H_2SO_4 , 95–98%) under vigorous stirring first at room temperature for 3 h and then at 45 °C for 8 h. The sulfonation reaction was stopped by precipitating the polymer solution into an ice-water bath. The obtained precipitate was washed repeatedly by de-ionized water until neutral pH was



Scheme 1. The molecular structure of Tiron.

reached. The sulfonated polymer was dried at room temperature for 24 h and at 60 °C under vacuum for another 24 h. The degree of sulfonation (DS) of SPEEK was determined to be 62% by acid–base titration.

2.3. Preparation of sulfonated titania submicrospheres

Titania submicrospheres (TiO_2) with a particle size of 220 nm were synthesized by a modified sol–gel method as described before [19]. For the sulfonation of TiO_2 , Tiron (molecular structure shown in Scheme 1) containing two $-\text{SO}_3\text{Na}$ groups per molecule was used as the sulfonation reagent. A facile chemical adsorption procedure was conducted [16,17]. The TiO_2 submicrospheres were first suspended into a HCl aqueous solution (pH 2.0) under ultrasonic treatment for 2 h, then poured into an excessive freshly prepared Tiron aqueous solution (4 mg mL^{-1} , pH 2.0). The suspension was vigorously stirred at room temperature for 30 min to allow a complete chemisorption of catecholic salt onto TiO_2 . The low pH prevented the catechol end groups of Tiron from oxidation, thus increasing the affinity of TiO_2 surface for Tiron. This strong affinity via chemical fixation would ensure the stability of the chelation structure in the practical acidic environment in DMFCs. The modified TiO_2 submicrospheres were rinsed with de-ionized water until neutral pH was reached. The as-synthesized sulfonated titania submicrospheres were dried at 80 °C for 24 h and denoted as $\text{TiO}_2\text{-SO}_3\text{H}$.

2.4. Preparation of membranes

SPEEK was dissolved in DMF under vigorous stirring at room temperature to get a homogeneous solution with a SPEEK concentration of 13 wt.%. The $\text{TiO}_2\text{-SO}_3\text{H}$ or TiO_2 was dispersed in DMF under ultrasonic treatment and stirring. The titania-DMF suspension was mixed with the SPEEK-DMF solution under vigorous stirring at room temperature. The mixture was cast onto a clean glass plate and dried at 60 °C overnight followed by further drying at 80 °C for 12 h. After being cooled down to room temperature, the membrane was peeled off from the glass plate. The resultant membranes were first immersed into 1 M HCl solution for 48 h to transform into acid form, and then rinsed with de-ionized water to remove residual HCl and dried at room temperature under vacuum. The as-prepared membranes were designated as SPEEK/ $\text{TiO}_2\text{-SO}_3\text{H-X}$ or SPEEK/ $\text{TiO}_2\text{-X}$, where X (=5, 10, 15 or 20) was the weight ratio of the fillers to SPEEK. Plain SPEEK membrane was also fabricated for comparison. The thickness of all of the membranes was within the range of 55–70 μm .

2.5. Characterizations

The morphology of the TiO_2 submicrospheres was characterized by transmission electron microscopy (TEM, JEOL). The cross-section morphology of the membranes was observed using field emission scanning electron microscope (FESEM, Nanosem 430) operated at 15 kV. The samples were prepared by freeze-fracturing in liquid nitrogen, and subsequently coated with a thin layer of sputtered gold.

The surface elemental composition of $\text{TiO}_2\text{-SO}_3\text{H}$ was analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI 1600 spectrometer with Mg $K\alpha$ radiation for excitation. Fourier transform infrared spectra (FTIR, $4000\text{--}400\text{ cm}^{-1}$) of the fillers and membranes were recorded on a Nicolet MAGNA-IR 560 instrument.

Thermogram curves (TGA, Perkin-Elmer Pyris) of the fillers and membranes were recorded in the temperature range of $20\text{--}800\text{ }^\circ\text{C}$ using a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen flow. The mechanical strength of the membranes was measured on Testometric 350 AX. The membrane samples were cut into $1.0\text{ cm} \times 4.0\text{ cm}$ and examined at an elongation rate of 4 mm min^{-1} at room temperature.

2.6. Swelling property

The swelling property of the membranes was determined by comparing the membrane area difference before and after soaking in water. A piece of dry, rectangular-shaped membrane ($4.0\text{ cm} \times 4.0\text{ cm}$) with an area of A_{dry} (cm^2) was immersed in water at $20, 30, 40, 50$ and $60\text{ }^\circ\text{C}$, respectively, for a period of time until the full hydration state was obtained, then the size of the membrane was re-measured (A_{wet} , cm^2). The swelling degree was determined by the average of three repeated measurements with an error within $\pm 3\%$ and calculated by Eq. (1)

$$\text{Swelling degree (\%)} = \frac{A_{\text{wet}} - A_{\text{dry}}}{A_{\text{dry}}} \times 100 \quad (1)$$

2.7. Ion-exchange capacity (IEC)

The IEC value of the membrane was measured using the back-titration method. The membrane in acid form was immersed in a 2 M NaCl solution for 48 h to completely replace the H^+ ions with the Na^+ ions followed by back-titration of the remaining solution with 0.01 M NaOH solution using phenolphthalein as an indicator. The IEC value was calculated according to Eq. (2)

$$\text{IEC (mmol g}^{-1}\text{)} = \frac{0.01 \times 1000 \times V_{\text{NaOH}}}{W_d} \quad (2)$$

where V_{NaOH} was the volume of NaOH solution consumed for titration and W_d was the weight of the dry membrane sample. The measurements were carried out with an accuracy of 0.001 mmol g^{-1} .

2.8. Methanol permeability

The methanol permeability was measured at room temperature using a glass diffusion cell [14,19]. The cell consisted of two compartments of identical volume separated by the membrane sheet. The membrane was fully hydrated in water for 24 h before test. One of the two compartments was filled with water and the other with 2 M methanol solution. The methanol concentration in the water compartment was monitored periodically using a gas chromatography (Agilent 6820) equipped with a thermal conductivity detector (TCD) and a DB624 column. The methanol permeability (P , $\text{cm}^2\text{ s}^{-1}$) was calculated according to Eq. (3)

$$P = S \frac{V_B l}{AC_{A0}} \quad (3)$$

where S was the slope of the straight line of concentration versus time; V_B was the volume of the receipt compartment; l , A , and C_{A0} were the membrane thickness, effective membrane area and feed

concentration, respectively. The measurement errors were within $\pm 4.0\%$.

2.9. Proton conductivity

The proton conductivity (σ , S cm^{-1}) of the membrane in the in-plane direction was measured at $25\text{ }^\circ\text{C}$ using a two-point-probe conductivity cell connected to a frequency response analyzer (FRA, Compactstat, IVIUM Tech.). The measurements were performed in a frequency range of $1\text{--}10^6\text{ Hz}$ with an oscillating voltage of 20 mV . All of the membranes were fully hydrated in water for 24 h prior to measurement. Three repeated measurements were conducted and averaged for each sample with an error within $\pm 5\%$. The proton conductivity was calculated by Eq. (4)

$$\sigma = \frac{l_0}{AR} \quad (4)$$

where l_0 and A were the distance between the two electrodes and the cross-sectional area of the membrane, respectively; R was the membrane resistance derived from the low intersection of the high frequency semicircle on a complex impedance plane with $\text{Re}(z)$ axis.

The overall membrane performance was evaluated by selectivity defined as the ratio of proton conductivity to methanol permeability.

3. Results and discussion

3.1. $\text{TiO}_2\text{-SO}_3\text{H}$ submicrospheres

Among various inorganic compounds, titania has been demonstrated as a suitable filler in synthesizing hybrid proton exchange membranes for its high hygroscopicity and chemical stability [8]. The addition of pristine TiO_2 submicrospheres and phosphorylated ones could enhance the methanol barrier property of membranes [19]. Herein, to further increase the proton conductivity and interfacial compatibility, the titania submicrospheres were modified with strong acidic groups (sulfonic acid groups) by Tiron agent through a chemical adsorption process.

The morphology of the titania submicrospheres (TiO_2) was observed by TEM as depicted in Fig. 1(a). The TiO_2 particles to be sulfonated were morphologically identical with an average particle size of $\sim 220\text{ nm}$. After sulfonation, the powder changed from white (the color of TiO_2) to dark-orange (the color of sulfonated TiO_2) as shown in Fig. 1(b), and no obvious change in size and morphology was observed. The obvious color change indicated the chemical adsorption of Tiron on the TiO_2 particles. The thermo gravimetric analysis was performed to determine the Tiron content on the titania (Fig. 1(c)). The weight loss in the temperature range of $170\text{--}650\text{ }^\circ\text{C}$ was attributed to the decomposition of Tiron and found to be approximately 15% , indicating a loading of $1.12\text{ mmol (-SO}_3\text{H) g}^{-1}\text{ TiO}_2\text{-SO}_3\text{H}$ particles.

The chemical structure and the surface chemistry of $\text{TiO}_2\text{-SO}_3\text{H}$ were probed by FTIR and XPS in Fig. 2. The as-prepared titania submicrosphere had a Ti-O-Ti main structure with the ethylene glycol molecules anchored on its surface by forming a dentate chelate form between glycol and Ti atoms [19]. In the FTIR spectrum shown in Fig. 2(a), the bands around 1640 cm^{-1} (the narrower one) and 3420 cm^{-1} (the broad one) corresponded to the scissoring vibration and the stretching vibration of adsorbed water molecules and hydroxyl groups on the surface, respectively [16]. The strong intensity of the band at 600 cm^{-1} was assigned to the Ti-O-Ti stretching vibration. Compared with the spectrum of TiO_2 , the characteristic peaks of ethylene glycol at 1080 cm^{-1} , 1400 cm^{-1} , 2868 cm^{-1} and 2930 cm^{-1} disappeared after sulfonation, and the characteristic peaks of Tiron appeared instead. The new sharp bands at

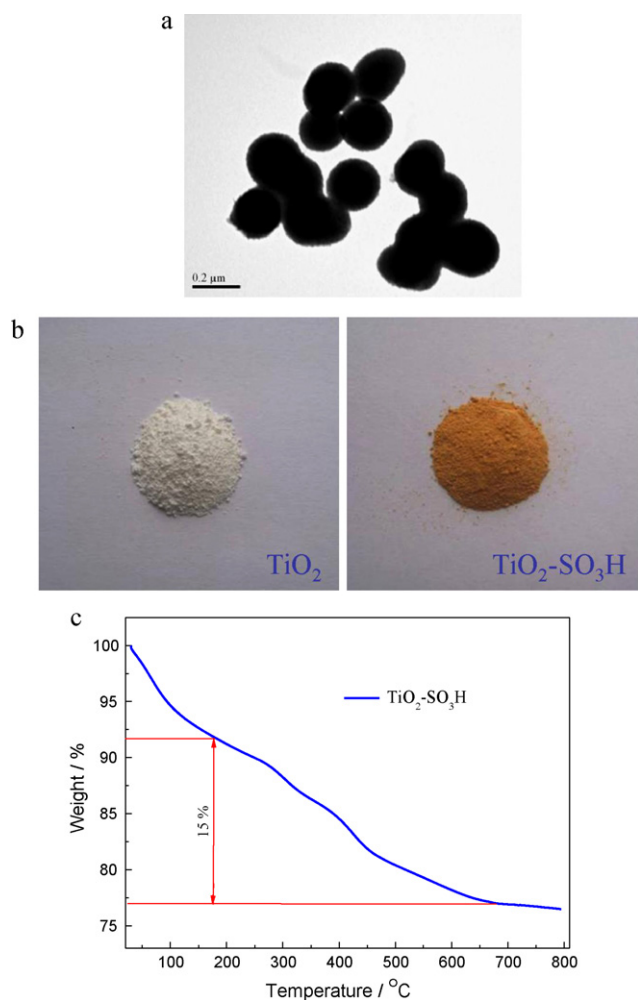


Fig. 1. TEM images of TiO_2 submicrospheres (a), photograph of the as-synthesized TiO_2 and $\text{TiO}_2\text{-SO}_3\text{H}$ powder (b) and TGA curve of the $\text{TiO}_2\text{-SO}_3\text{H}$ particles (c).

1030 cm^{-1} , 1180 cm^{-1} and 1270 cm^{-1} could be attributed to the symmetric stretching frequency of the SO_3^- , S–O vibration and S=O stretching vibrations, respectively. The bands at 1460 cm^{-1} were assigned to the C=C benzene ring characteristic vibrations [20]. Furthermore, the intensity of the characteristic peaks of the adsorbed water molecules and hydroxyl groups became stronger due to the higher surface hydrophilicity generated by the additional $-\text{SO}_3\text{H}$ groups [17]. It could be deduced from these results that Tiron replaced the original chelate position of glycol as a result of the catechol end groups of the Tiron bound covalently with the Ti atom at the titania surface.

The binding complexion of Tiron and TiO_2 was further explored with XPS analysis, and high-resolution O(1s) XPS spectra of clean TiO_2 surfaces and sulfonated TiO_2 surfaces was shown in Fig. 2(b). For pristine TiO_2 , as described in our previous work, the O(1s) spectra could be deconvoluted into two peaks (bottom): the stronger peak at 532.2 eV was attributed to the oxygen in the C–O–Ti bond, and the weaker peak at 529.8 eV corresponded to the oxygen in the Ti–O–Ti bond [21], indicating that ethylene glycol was attached to the TiO_2 surface via the formation of C–O–Ti covalent bonds. After sulfonation, the ethylene glycol was replaced with Tiron which was consistent with the result of FTIR. However, for the $\text{TiO}_2\text{-SO}_3\text{H}$ (top), it could be observed that the strong peak (532.0 eV) corresponded to the oxygen in the C–O–Ti bond shifted to lower binding energy by 0.2 eV rather than disappeared. It was attributed to the fact that the reaction between the catechol end groups and the

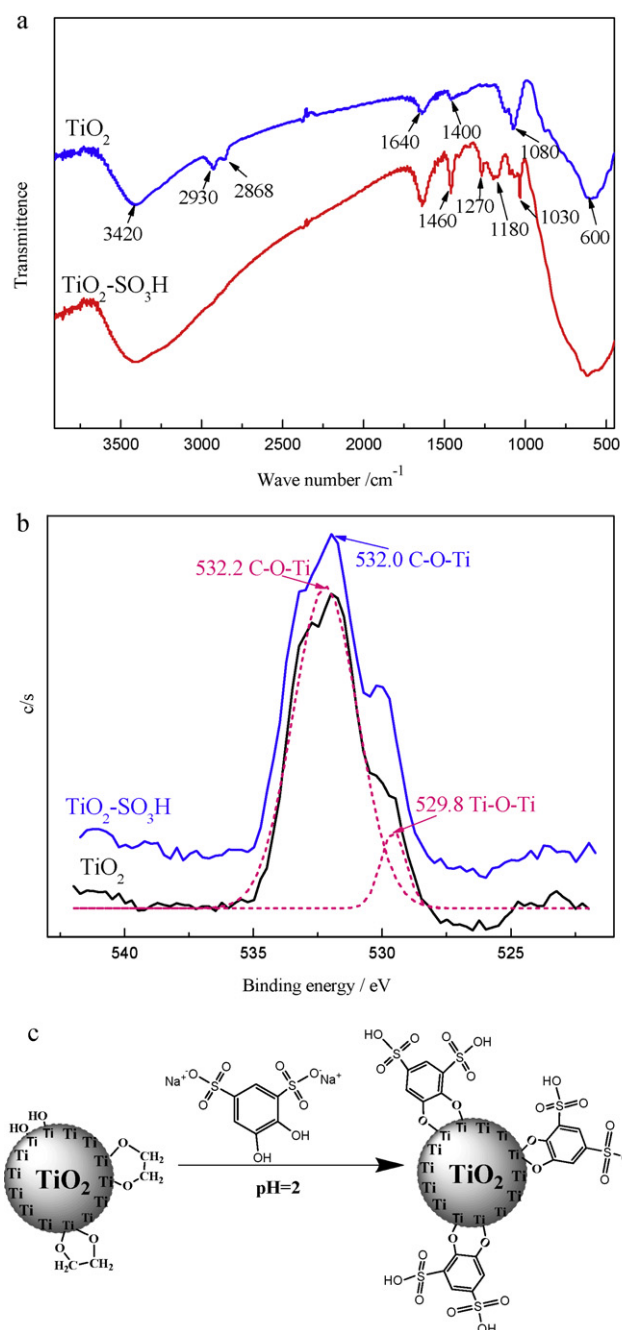


Fig. 2. FTIR spectra (a) and XPS spectra (b) of O 1s of $\text{TiO}_2\text{-SO}_3\text{H}$ and TiO_2 , sulfonic acid functionalization of TiO_2 (c).

Ti surface resulted in the formation of new C–O–Ti bonds. Furthermore, the peak at 529.8 eV corresponded to the oxygen in the Ti–O–Ti bond was still weaker, indicating that Tiron was attached to a majority of the TiO_2 surface. Based on the above characterization results, the sulfonation process could be tentatively illustrated in Fig. 2(c).

3.2. Characterizations of the hybrid membranes

The hybrid membranes having different filler contents were prepared via a solution casting method. Fig. 3 shows the representative photographs of the pristine SPEEK membrane and the SPEEK/ $\text{TiO}_2\text{-SO}_3\text{H}$ membrane. The membranes were transparent and the membrane color changed from colorless to yellow after

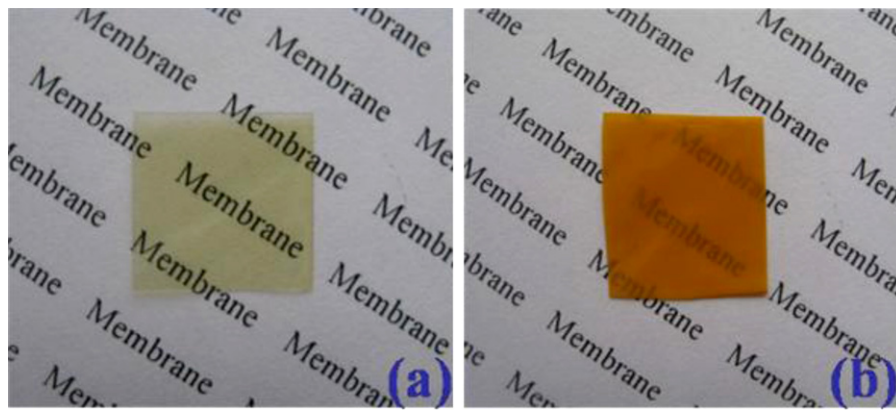


Fig. 3. Photographs of the representative membranes: the pristine SPEEK (a) and the SPEEK/TiO₂-SO₃H-15.

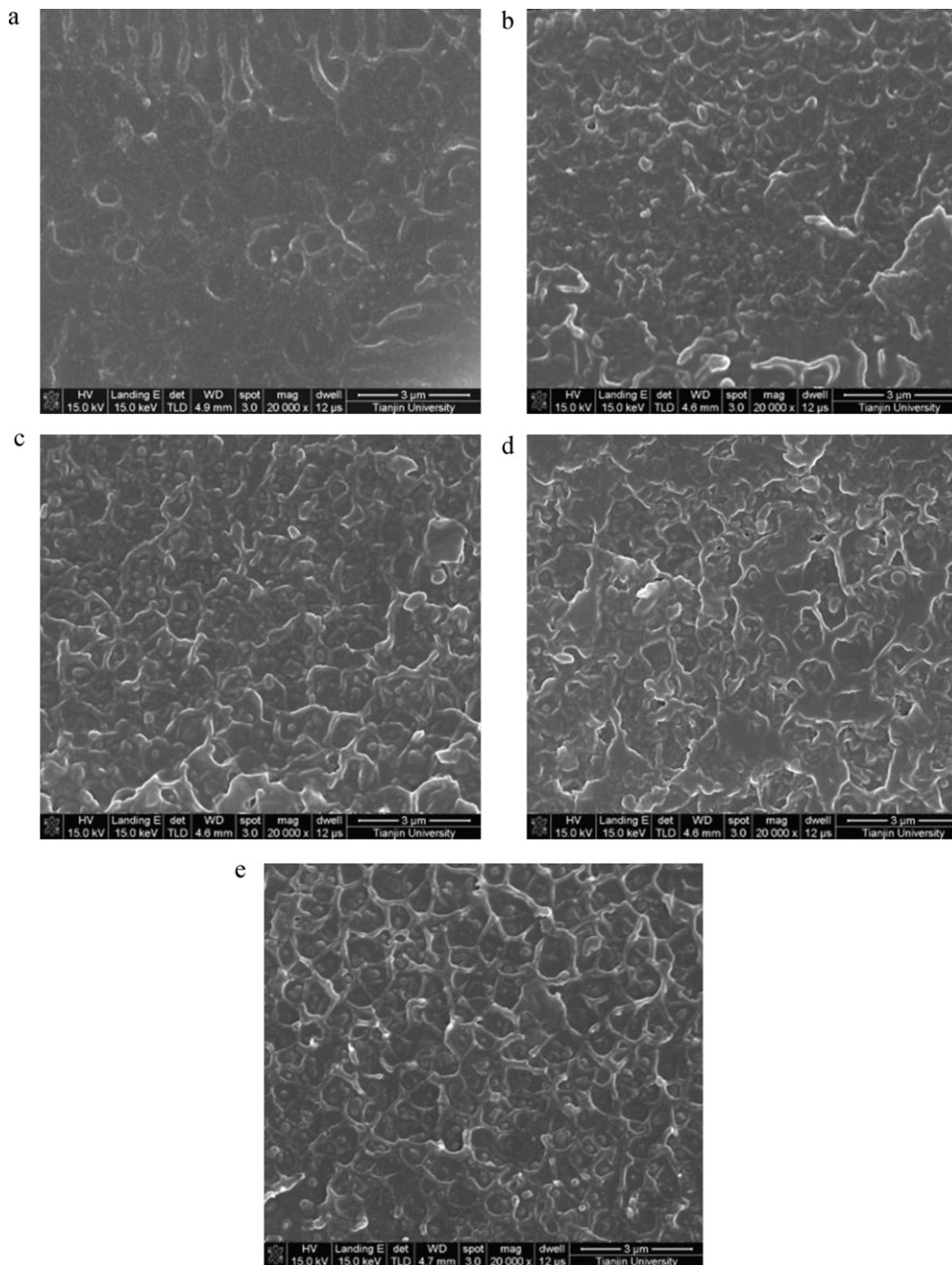


Fig. 4. FESEM images of the cross-section of SPEEK and SPEEK/TiO₂-SO₃H hybrid membranes: SPEEK (a), SPEEK/TiO₂-SO₃H-5 (b), SPEEK/TiO₂-SO₃H-10 (c), SPEEK/TiO₂-SO₃H-15 (d) and SPEEK/TiO₂-SO₃H-20 (e).

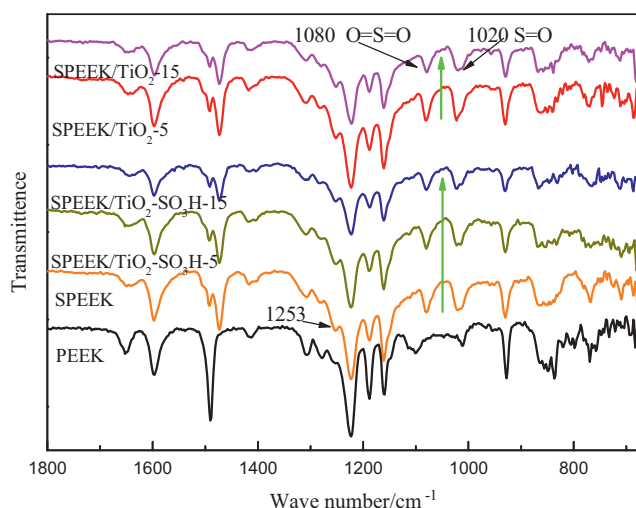


Fig. 5. FTIR spectra of PEEK, SPEEK and hybrid membranes.

incorporation of the yellow-colored $\text{TiO}_2\text{-SO}_3\text{H}$ fillers. The internal microstructure and the dispersion of the $\text{TiO}_2\text{-SO}_3\text{H}$ within the membrane were investigated by FESEM and the images of the cross-section of the $\text{SPEEK/TiO}_2\text{-SO}_3\text{H-X}$ membranes were shown in Fig. 4. The images revealed that no obvious $\text{TiO}_2\text{-SO}_3$ submicrospheres agglomeration occurred and the fillers were homogeneously distributed in the SPEEK matrix without structural defects. Such result could be reasonably attributed to the fact that the surface-modification with Tiron ligands having negatively charged terminal sulfonic groups resulted in a strong electrostatic repulsive force between the particles and the interaction between the fillers and SPEEK such as hydrogen bonds. The compatibility between the polymer and the inorganic fillers could potentially improve the membrane properties and performance [22].

The sulfonation process of the PEEK and the interfacial interaction between the fillers and polymer matrix were confirmed qualitatively by FTIR. From Fig. 5, compared to pure PEEK, three new absorption bands in the spectrum of SPEEK could be observed at 1020, 1080 and 1253 cm^{-1} , which corresponded to the characteristic peaks of the sulfonic groups assigned to asymmetric $\text{O}=\text{S}=\text{O}$ stretching, symmetric $\text{O}=\text{S}=\text{O}$ stretching, $\text{S}=\text{O}$ stretching, respectively [23]. After the incorporation of the fillers, strong and rich hydrogen bonds were generated between the $\text{-SO}_3\text{H}$ groups on the SPEEK and the hydrophilic groups on the particles, resulting in a decrease in the intensity of the characteristic peaks of $\text{-SO}_3\text{H}$ groups. Furthermore, the intensity of these characteristic peaks decreased as both of the TiO_2 and $\text{TiO}_2\text{-SO}_3$ content increased, suggesting an increase of interfacial interactions between the fillers and SPEEK.

3.3. Thermal and mechanical stabilities of the hybrid membranes

Thermal and mechanical properties are crucial for the proton exchange membrane to guarantee a long lifetime of the fuel cells [22]. The thermal stability of the SPEEK and the hybrid membranes was analyzed by TGA as illustrated in Fig. 6(a). It seemed that all the SPEEK-hybrid membranes as well as the pristine SPEEK membrane exhibited a similar three-step degradation pattern, which was consistent with the literature [8]. The first weight loss region (30–150 °C) could be attributed to the evaporation of adsorbed water and residual solvent; the second weight loss region around 360 °C was assigned to the decomposition of the sulfonic groups. In this region, the weight loss of the hybrid membranes was a

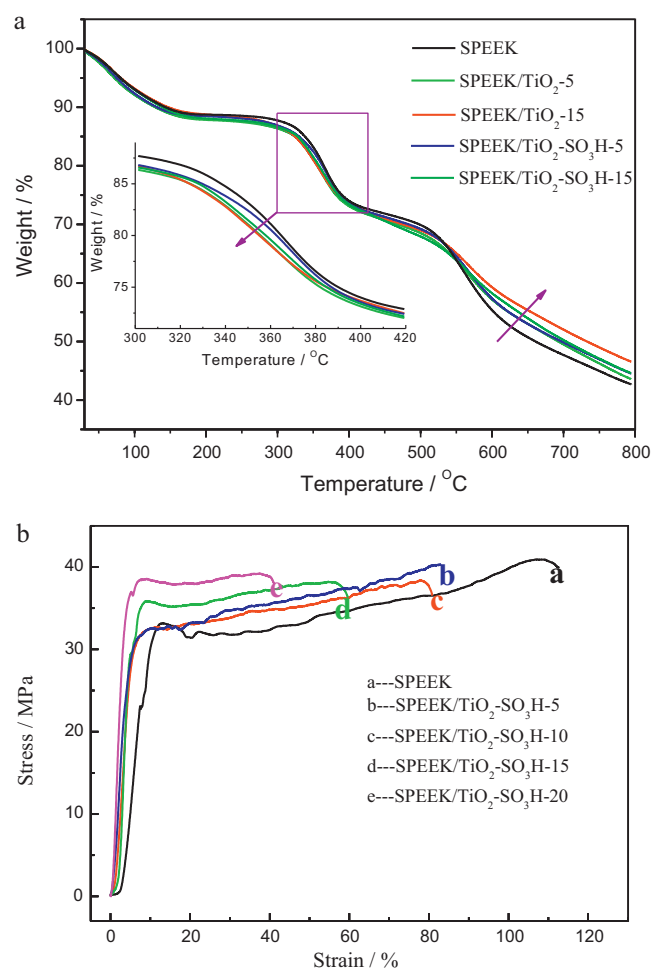


Fig. 6. TGA thermodiagram (a) and stress-strain curves (b) of SPEEK and hybrid membranes.

little higher than that of the pristine SPEEK membrane, which was mainly attributed to the fact that the surface functionalized sulfonic groups of TiO_2 was also thermally decomposed in this temperature region [24]. The third weight loss with the onset temperature at about 520 °C corresponded to the degradation of the polymer backbone. In this region, compared to the pristine SPEEK membrane, the presence of inorganic fillers retarded the oxidative degradation of SPEEK main chains, leading to an improvement in the membrane thermal stability. It should be pointed that the hybrid membranes were thermally stable below 300 °C and met the temperature requirement for DMFC operation.

The mechanical properties of the hybrid membranes were measured with an Instron, and the stress-strain curves of the hybrid membranes were shown in Fig. 6(b). The pristine SPEEK with a Young's modulus of 542.86 MPa and an elongation at break of 110% showed good ductility. For the hybrid membranes, both the tensile strength and the Young's modulus increased with the increase of the $\text{TiO}_2\text{-SO}_3\text{H}$ content from 5 wt.% to 20 wt.%. Especially, the Young's modulus increased remarkably from 687.59 MPa to 1371.41 MPa, indicating a significant improvement in mechanical strength. However, as the content of $\text{TiO}_2\text{-SO}_3\text{H}$ increased, the elongations at break decreased from 82% to 40%. This phenomenon originated from the rigidity of the inorganic fillers which restricted the polymer chain segmental mobility and enhanced the rigidity of resulted membranes [25]. The mechanical properties of the hybrid membranes were good enough for application in DMFCs.

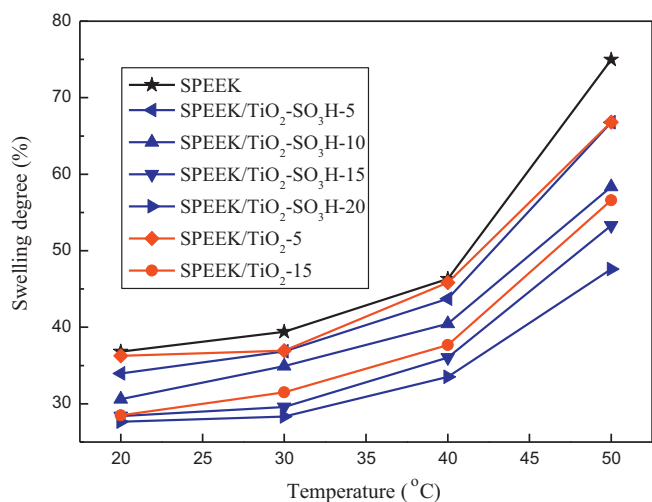


Fig. 7. Area swelling degree of SPEEK and hybrid membranes at different temperatures.

3.4. Swelling behavior of the hybrid membranes

The membrane dimensional swelling is an important parameter for DMFC applications, especially for most sulfonated hydrocarbon polymer membranes with a high DS. High swelling property can exert a blight effect on the membrane performance by reducing its methanol-rejecting ability and mechanical strength. The area swelling degree of the SPEEK and hybrid membranes at different temperatures were plotted in Fig. 7. As temperature increased, the area swelling degree of all membranes increased. It was noteworthy that the hybrid membranes exhibited a lower swelling degree compared to the pristine SPEEK with a relatively high DS of 62%, probably due to the less hydrophilic character of the fillers and the reduced free volume in the polymer membranes caused by the additional interaction between SPEEK and fillers [4,26]. The area swelling degree of the membranes decreased from 75.0% to 47.6% as the amount of the $\text{TiO}_2\text{-SO}_3\text{H}$ increased from 0% to 20% at 50 °C, and the hybrid membranes incorporated with TiO_2 showed a similar tendency. This result indicated that incorporation of the inorganic fillers was propitious to the membrane size stability. However, at the same fillers content, the swelling degree of the SPEEK/ $\text{TiO}_2\text{-SO}_3\text{H}$ hybrid one was slightly lower than that of SPEEK/ TiO_2 [27]. At 60 °C (data not shown), the membranes absorbed too much water and swelled seriously.

3.5. IEC and proton conductivity

Proton conductivity is one of the most important properties of DMFC membranes. Ion-exchange capacity (IEC) was an indicator of the density of dissociable hydrophilic functional groups and available protons in the membrane. The IEC values of the membranes synthesized were determined by titration method and shown in Fig. 8. The pristine SPEEK membrane exhibited an IEC value of $\sim 1.8 \text{ mmol g}^{-1}$, and the corresponding DS was calculated to be 62%. For the hybrid membranes, the IEC values of SPEEK/ $\text{TiO}_2\text{-SO}_3\text{H}$ and SPEEK/ TiO_2 both decreased with the increase of filler content, and the IEC value for SPEEK/ $\text{TiO}_2\text{-SO}_3\text{H}$ was higher than that for SPEEK/ TiO_2 . This was presumably due to the fact that the fillers with a lower IEC compared with SPEEK diluted the concentration of sulfonic acid groups and the sulfonic acid groups of $\text{TiO}_2\text{-SO}_3\text{H}$ provided some compensation to the IEC value reduction [10,19].

The proton conductivity of the membranes measured at room temperature was also shown in Fig. 8. The pristine SPEEK membrane with a relatively high DS showed a high proton conductivity

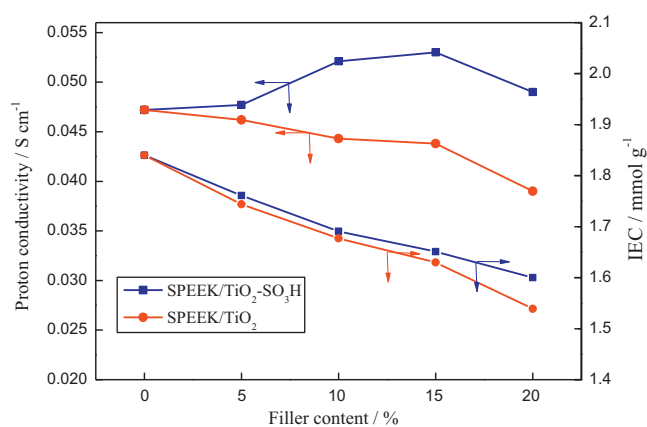


Fig. 8. IEC values and proton conductivity of SPEEK and hybrid membranes.

of 0.047 S cm^{-1} . Compared with SPEEK membrane, the proton conductivity of SPEEK/ $\text{TiO}_2\text{-SO}_3\text{H}$ membranes increased from 0.048 S cm^{-1} to 0.053 S cm^{-1} with the $\text{TiO}_2\text{-SO}_3\text{H}$ content increasing from 5 wt.% to 15 wt.%. When the $\text{TiO}_2\text{-SO}_3\text{H}$ content reached 20 wt.%, a decrease in proton conductivity was observed. The proton conductivity of the SPEEK/ TiO_2 hybrid membranes decreased gradually from 0.046 to 0.039 S cm^{-1} as the filler content increased from 5 wt.% to 20 wt.%. It could be clearly seen that the proton conductivity of the hybrid membranes was improved by sulfonation of the TiO_2 particles. The enhanced proton conductivity by embedding with $\text{TiO}_2\text{-SO}_3\text{H}$ was probably contributed to both the vehicle mechanism and the Grotthuss mechanism [26,28]. On one hand, the additional sulfonic groups on the TiO_2 surface promoted surface hydrophilicity resulting in adsorbing more water molecules by formation hydrogen bonds, which facilitated the vehicle mechanism by contributing to continuous hydrophilic regions/pathways. On the other hand, after sulfonation, the titania particles contained substantial amounts of sulfonic acid groups, and the density of sulfonic acid groups at the interface of TiO_2 and SPEEK was increased. Thereby, the protons were likely to be transported along the surface and/or the edges of the particles by jumping from one $\text{-SO}_3\text{H}$ group to another. The homogeneously dispersed $\text{TiO}_2\text{-SO}_3\text{H}$ within the SPEEK matrix induced a new proton transfer pathway, leading to an increase in the proton conductivity.

3.6. Methanol permeability and selectivity

Methanol crossover through the membrane is a critical problem in DMFC applications, as it will directly lead to an open-circuit potential drop and a reduction in fuel utilization efficiency [23]. The methanol transport through the membrane in a DMFC is driven by both the concentration gradient and the electro-osmotic drag between the anode and cathode. The hydrophilic channels in SPEEK have been found to be narrower and more branched than that in Nafion[®], leading to a lower electroosmotic drag and permeation coefficient [29,30]. Herein, the diffusion contribution was measured and expressed in terms of methanol permeability (P , $\text{cm}^2 \text{ s}^{-1}$). The methanol permeability of the SPEEK and the hybrid membranes at room temperature were presented in Fig. 9(a). The methanol permeability of the pristine SPEEK membrane was found to be $5.72 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and that of the hybrid ones decreased dramatically with increasing filler contents. Compared to the pristine SPEEK membrane, as the fillers content increased from 5 wt.% to 20 wt.%, the methanol permeability decreased by 10.0% to 33.7% for SPEEK/ TiO_2 membranes and by 17.7% to 36.2% for SPEEK/ $\text{TiO}_2\text{-SO}_3\text{H}$ membranes, respectively. The presence of fillers reduced the methanol crossover through the membrane for the

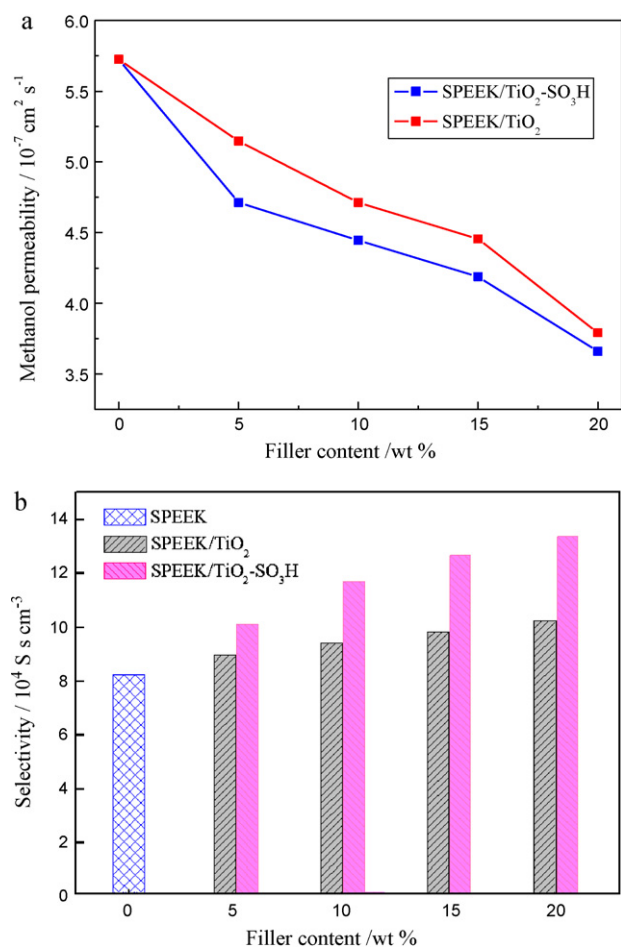


Fig. 9. Methanol permeability (a) and selectivity (b) of SPEEK and hybrid membranes.

following reasons. The strong interaction between the fillers and SPEEK inhibited the polymer chain mobility, which reduced the free volume of the hybrid membrane, so as to reduce the channel size for methanol molecules passing through the membrane [10,31]. Moreover, the inorganic fillers were impermeable for methanol and hence the presence of the fillers within the bulk polymer matrix obstructed and twisted the methanol diffusion pathway [7,24]. All these factors increased the diffusion resistance and consequently suppressed the methanol crossover. Compared with the SPEEK/TiO₂ membranes, the TiO₂-SO₃H embedded hybrid membranes displayed lower methanol permeability. This reduction was ascribed to the fact that TiO₂-SO₃H particles enhanced the interaction between the organic and inorganic phases and thus resulting in better interfacial compatibility. The improved interfacial morphology minimized the occurrence of nonselective voids and pores [10,25,32].

The desired membrane materials for DMFC application must possess high proton conductivity and low methanol permeability simultaneously. A parameter, usually termed as selectivity, defined as the ratio of proton conductivity to methanol permeability, is commonly used as a barometer to evaluate the overall membrane performances. The selectivity of the as-prepared membranes in this study was shown in Fig. 9(b). The selectivity of the hybrid membranes increased with increasing filler contents. The SPEEK/TiO₂ hybrid membranes had a slightly higher selectivity in comparison with the SPEEK membrane, which was mainly due to the enhanced methanol barrier property. The SPEEK/TiO₂-SO₃H hybrid membranes displayed the highest selectivity, owing

to both increased proton conductivity and reduced methanol permeability.

Generally, the relationship of proton conductivity and methanol permeability was interdependent and interinhibitive for polymer membranes. There often exists a “trade-off” phenomenon between these two indices. Organic–inorganic hybrid membranes may provide an effective approach to cross this hurdle. Herein, the TiO₂-SO₃H microspheres homogeneously dispersed within the SPEEK matrix not only constructed additional proton transfer pathways but also optimized the interfacial morphology, thus leading to a simultaneous improvement in both proton-conducting ability and alcohol-rejecting property.

4. Conclusions

In this study, titania submicrospheres with sulfonic acid groups on their surfaces were synthesized through a facile and fast surface-functionalization approach via chelation reaction. The sulfonated titania submicrospheres were then incorporated into SPEEK matrix to get a series of hybrid membranes. The influence of the fillers on the properties and performances of SPEEK membranes were extensively characterized by FTIR, FESEM, TGA, mechanical test, swelling, methanol crossover and proton conductivity. The additional sulfonic acid groups on the TiO₂ strengthened the interactions and improved the interfacial compatibility between the inorganic filler and the polymer matrix, therefore the SPEEK/TiO₂-SO₃H hybrid membranes displayed improved dimensional stability and methanol resistance. It was found that the hybrid membranes showed an increase in mechanical strength with increasing TiO₂-SO₃H content. The SPEEK/TiO₂-SO₃H hybrid membranes displayed higher proton conductivity and lower methanol permeability, resulting in a higher selectivity in comparison with the pristine SPEEK membrane and the SPEEK/TiO₂ membrane. The last but not least point is that the methanol crossover driven by the electro-osmotic drag besides the concentration gradient should also be taken into account in view of practical DMFC applications.

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