Journal of Power Sources 196 (2011) 6015–6021

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Lamellar crystals as proton conductors to enhance the performance of proton exchange membrane for direct methanol fuel cell

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ARTICLE INFO

Article history:
Received 2 March 2011
Received in revised form 6 April 2011
Accepted 6 April 2011
Available online 12 April 2011

Keywords:
Zirconium glyphosate
Sulfonated polyether ether ketone
Proton conduction
Hybrid membrane
Direct methanol fuel cell

ABSTRACT

Zirconium glyphosate (ZrG) is a solid proton conductor with layered crystal structure. The inorganic veneer sheets of ZrG are covalently intercalated by glyphosate molecules with carboxylic acid end groups (–COOH). The existence of abundant –COOH groups both inside and on the surface of ZrG provides additional proton-conducting channels facilitating the proton conduction through and around the inorganic crystals. ZrG is incorporated into the sulfonated polyether ether ketone (SPEEK) matrices to prepare proton-conducting hybrid membranes. The conductivity of the hybrid membranes is higher than the pristine SPEEK membrane, and increases with increasing ZrG content. Furthermore, the enhancement of the proton conductivity is more obvious at elevated temperatures. At 25 °C, the proton conductivity of the hybrid membrane with 16 wt% ZrG is 1.4 times higher than that of the pristine membrane. When the temperature increases to 55 °C, the conductivity of the hybrid membrane with 8 wt% ZrG is more than twice that of the pristine SPEEK membrane. The prolonged and tortuous pathways originated from the incorporation of inorganic crystals lead to reduced methanol permeability. The selectivity of the hybrid membrane is increased by as much as 72% compared to the pristine SPEEK membrane.

1. Introduction

Direct methanol fuel cell (DMFC) is one of the most promising candidates especially for portable devices and transportation applications because of its high energy efficiency as well as simple system design and operation conditions [1,2]. Proton exchange membrane (PEM) which serves as the heart of a DMFC should have some principal features including high proton conductivity, low methanol permeability, reasonable long-term chemical, thermal and hydrolytic stability, low cost and ready availability, etc. [1,3]. The development of organic–inorganic hybrid membranes through introduction of inorganic phases into polymer matrices either by direct blending with inorganic fillers or by in situ sol–gel processes provides an efficient solution to tackle these challenges [1–5]. Zirconium phosphate (ZrP) is an attractive candidate for its hygroscopic and solid acid proton conductive property. It could provide abundant proton conducting sites to compensate for the proton conductivity loss caused by the incorporation and its hydrophilic nature could promote the water retention capacity at elevated temperature or low humidity [6]. Similar to other kinds of layered materials such as clay, montmorillonite and silicate, zirconium phosphate was dispersed in organic matrix in three typical states: (1) crystal or amorphous filler neither be intercalated nor be exfoliated, such as α-zirconium phosphate nano-particles [7,8] and mesoporous zirconium phosphate [9]; (2) lamellar crystal intercalated by the polymer chains like zirconium meta-sulfonphenyl phosphonic acid [10,11] and polybenzimidazole-modified zirconium phosphate [12]; (3) crystals that were exfoliated into several layers or even one layer per crystal filler, such as amino-modified zirconium phosphate [13–15].

The introduction of functional groups such as sulfonic acid groups, carboxylic acid groups and phosphoric acid groups into the inorganic phase is a promising way to improve the proton-conducting ability of organic–inorganic hybrid membranes. Besides the syntheses of novel materials with high ion-exchange-capacity (IEC), the construction of regular and continuous proton-conducting channels in the membrane is of additionally crucial significance to enhance proton conductivity. Nafion® series membranes have been successfully utilized in hydrogen proton-exchange membrane fuel cells especially for their high proton conductivity under sufficiently hydrated state. The Nafion® membrane structure is featured by the phase separation between the poly-tetrafluoroethylene backbone and the regularly spaced perfluorovinyl ether side-chains (hydrophobic domains) each terminated by a strongly hydrophilic sulfonate ionic group (hydrophilic domains). Their high conductivity is assigned

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doi:10.1016/j.jpowsour.2011.04.014

to the continuous charge passages, the well-connected proton-conducting channels, in the membrane where the hydrated protons (H_3O^+) serve as protonic charge carriers. Leem et al. constructed proton-conducting channels throughout the membranes by filling amino acid-functionalized silica particles into the trans-membrane pores of porous membranes [16]. Tamura and Kawakami created continuous proton-conducting channels by the incorporation of uniaxially aligned sulfonated polyimide nanofibers into sulfonated polyimide [17].

Zirconium glyphosate (ZrG) is a lamellar crystal with an abundant amount of aminoacetic acid residues both on the surface and inside the interlayer. This layered compound was first synthesized by Xu et al. using zirconyl chloride octahydrate ($ZrOCl_2·8H_2O$) and N-(phosphonomethyl)glycine (glyphosate, Gly) [18]. ZrG exhibited a high crystallinity with a *d*-spacing of ~1.645 nm. The crystal was intercalated by glyphosate molecules terminated by acid groups (carboxylic acid, –COOH) in a head-to-head mode. In view of the lamellar crystal nature and the organic-modified structure of ZrG, it is reasonable to expect that the incorporation may provide a novel approach to achieve an enhanced alcohol barrier property without sacrificing proton conductivity by constructing additional proton-conducting channels within the hybrid membrane. In the present study, the glyphosate-inercalated ZrG was synthesized and incorporated into sulfonated polyether ether ketone (SPEEK) to prepare proton conductive membranes with enhanced alcohol barrier property.

2. Experimental

2.1. Materials and chemicals

Glyphosate (>95 wt%) was generously donated by Weihai Hanfu Biological and Chemical Medication Co., Ltd. Zirconyl chloride octahydrate (99.99 wt% (metals basis)) and polyether ether ketone (Victrex PEEK 381G) were purchased from Shanghai Zenith Company and Vitrex England, respectively. All the other reagents were commercially available with analytically pure degree, and used as received. De-ionized water was used in all the experiments.

2.2. Preparation of ZrG and SPEEK

The synthesis of ZrG was carried out according to the procedure presented in the literature [18]. Aqueous solutions of glyphosate (0.05 M) and Zr^{4+} (0.3 M) were prepared by dissolving glyphosate and $ZrOCl_2·8H_2O$ in water, respectively. HF solution (40 wt%, 3 mL) was added into the Zr^{4+} solution (30 mL) dropwise under stirring. Then the above mixture was dropped into 360 mL glyphosate at 70 °C and refluxed for 6 h. The resultant suspension was filtered, rinsed thoroughly with water, and dried at 80 °C for 24 h.

SPEEK was prepared by sulfonation of PEEK [19]. PEEK was dried at 120 °C for 24 h and then dissolved in concentrated sulfuric acid at 0 °C under agitation for 24 h. Then the solution was heated to 45 °C and kept under stirring for another 8 h. Dark red precipitation was recovered immediately after decanting the solution into a large excess of water. The crude product was washed with water until pH 7 and dried at 80 °C for 24 h. The sulfonation degree (DS) of the as-synthesized SPEEK was determined to be 41.8% through a back-titration method.

2.3. Preparation of the pristine SPEEK membrane and the SPEEK/ZrG hybrid membranes

SPEEK was dissolved in N,N-dimethyl formamide (DMF) under stirring at room temperature to get a concentration of 10 wt%. Then ZrG was added into the solution under rigorous stirring for 30 min and then treated by ultrasonication for 15 min. The SPEEK/ZrG membranes were prepared by casting the above mixture on clean glass plates followed by drying first at 60 °C for 6 h and then at 80 °C for another 6 h. The dry membranes were immersed in 1 M H_2SO_4 to be acidified, washed thoroughly by water and dried again at 80 °C. The as-prepared membranes were denoted as SPEEK/ZrG-Z%, where Z referred to the weight percentage of ZrG relative to SPEEK.

2.4. Characterizations

Scanning electron microscopy (SEM) images were obtained on a Philips XL30 at 20.0 kV. The ultrasonic-dispersed ZrG-methanol suspension was dropped on a glass slide and observed after solvent evaporation.

The crystallinity of ZrG was detected by X-ray diffraction (XRD) (RigakuD/max2500 v/pc, Japan, CuKα radiation). The Cu–X ray source ($\lambda = 0.154056$ nm) operated at 40 kV and 200 mA. The diffraction patterns were recorded over a 2θ range of 3–60° at a rate of $5^\circ\ \text{min}^{-1}$.

The Fourier transform infrared spectra (FTIR) of ZrG (1800–400 cm^{-1}) and SPEEK/ZrG membranes (2000–670 cm^{-1}) were recorded using a Nicolet-560 spectrometer at 4 cm^{-1} resolution.

Thermal gravimetric analyses (TGA) of ZrG and SPEEK/ZrG hybrid membranes were conducted using a TA-50 thermal gravimetric analyzer (Shimadzu, Japan) under nitrogen atmosphere at a flow rate of 30 mL min^{-1}. The dry samples were heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1}.

2.5. Water uptake, area swelling, sulfonation degree and Ion-exchange-capacity

The membranes were dried at room temperature in vacuum for 24 h, weighed (W_{dry}) and measured (A_{dry}, the area of the dry membranes), and then immersed in water at 25 °C for 24 h. The wet membranes were taken out, blotted with filter papers to remove the water residues on the surface, weighed (W_{wet}) and measured (A_{wet}) again. The measurements were repeated three times and the error was within ±5%. The water uptake and swelling were calculated according to the following equations (Eqs. (1) and (2)), respectively:

$$\textit{water uptake}\,(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

$$\textit{swelling}\,(\%) = \frac{A_{wet} - A_{dry}}{A_{dry}} \times 100 \tag{2}$$

The sulfonation degree of SPEEK was determined by back-titration [20]. SPEEK was dried, weighed and immersed in a 0.1 M NaOH solution for 24 h. The solution was back-titrated to neutral with a 0.1 M HCl solution using phenolphthalein as an indicator. The IEC of SPEEK was calculated as follows (Eq. (3)):

$$EW = \frac{1000}{IEC} = \frac{m}{V_{NaOH} \times C_{NaOH} - V_{HCl} \times C_{HCl}} \tag{3}$$

where m was the weight of dry SPEEK (g); V_{NaOH} and C_{NaOH} were the volume (mL) and concentration (mol L^{-1}) of the NaOH solution, respectively; V_{HCl} and C_{HCl} were the volume (mL) and concentration (mol L^{-1}) of the HCl solution, respectively.

DS was calculated according to Eq. (4):

$$DS\% = \frac{M_{SPEEK}}{(1/IEC) - M_{-SO3H}} \times 100 \tag{4}$$

where M_{SPEEK} and M_{-SO3H} were the molecular weight of the SPEEK monomer repeat unit (288 Da) and the sulfonic acid group (81 Da), respectively.

2.6. Methanol permeability

Methanol permeability was measured using a glass diffusion cell as described in the literatures [1,21]. It consisted of two compartments (A and B) in identical volume separated by the membrane. The compartment A was filled with methanol (5 M) and B was filled with water. The methanol permeability was determined by analyzing the concentration of methanol in compartment B using gas chromatography (Agilent 6820) equipped with a TCD detector and a DB624 column. The methanol permeability (P, cm^2 s^{-1}) was calculated from Eq. (5):

$$P = S\frac{V_B l}{AC_{A0}} \tag{5}$$

where S was the slope of the straight line of methanol concentration in compartment B versus time; V_B was the volume of compartment B; l and A were the thickness and the effective area of the membrane, respectively; C_{A0} was the initial methanol concentration in compartment A.

2.7. Proton conductivity

The in-plane proton conductivity of the membrane was determined with a two-point-probe conductivity cell [1,22]. The data were collected by AC impedance spectroscopy (Autolab PGSTST20, The Netherlands) using a frequency response analyzer (Parstat2273 Advanced Electrochemical System, FRA, Compactstat, IVIUM Tech.) over a frequency range of 1–10^6 Hz with an oscillating voltage of 20 mV. The membrane samples were fully hydrated by water before the measurements. The proton conductivity σ (S cm^{-1}) was calculated by the following equation:

$$\sigma = \frac{l}{AR} \tag{6}$$

where l was the distance between the two electrodes; A was the effective cross-sectional area of the membrane sample; R was the measured membrane resistance.

3. Results and discussion

3.1. Characterizations of ZrG

The SEM image of the as-synthesized ZrG was shown in Fig. 1(a). The solid compound of ZrG was composed of long lamellas in strip form with a length of about 900 nm and a width of about 100 nm. The crystal structure was detected by XRD pattern as shown in Fig. 1(b). The sharp diffraction peaks with narrow widths confirmed the high crystallinity of ZrG. The interlayer spacing between the inorganic veneer sheets was ~1.645 nm calculated from Bragg equation, according to the most intensive peak at 5.37° relative to the crystal surface (0 0 2) [18]. The thickness of the inorganic sheet was 0.240 nm, the length of the glyphosate molecular chain was 0.730 nm, therefore, the theoretical interlayer spacing was calculated to be 1.700 nm [18,23,24]. The small difference between the calculated d-spacing (1.700 nm) and the measured one (1.645 nm) indicated the attractive interactions between the two head-to-head glyphosate molecules via hydrogen bonds. The head-to-head glyphosate molecules between the inorganic sheets formed a network of hydrogen bonds which served as proton-conducting channels, and thus facilitating the migration of protons. The glyphosate molecule itself may also form a five-membered hydrogen-chelating ring via intramolecular hydrogen bond.

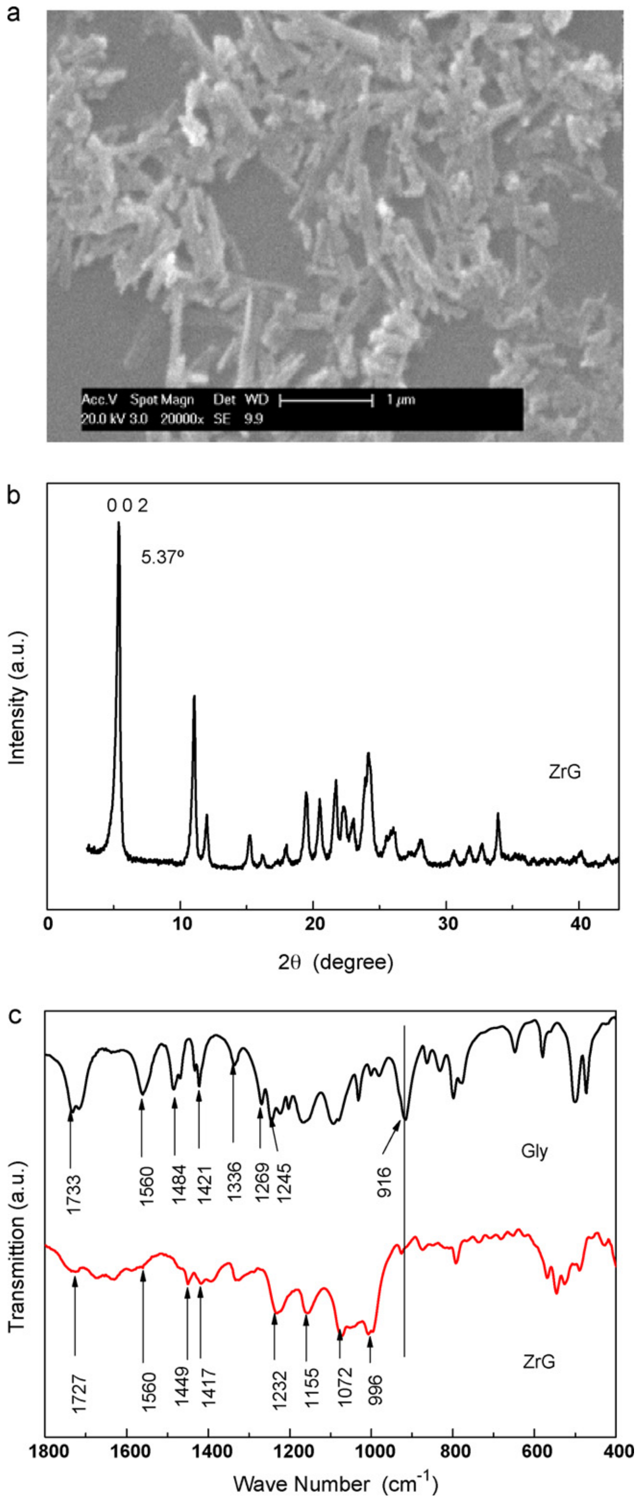

Fig. 1. Characterizations of ZrG: (a) SEM image, (b) XRD pattern, and (c) FTIR spectra.

The chemical structure of ZrG was further elucidated by FTIR spectra (Fig. 1(c)). The stretching motions of $\nu_{\text{C–OH(COOH)}}$ (1417 cm^{-1} in ZrG; 1421 cm^{-1} in Gly), $\nu_{\text{–CH2}}$ (1232, 1449 cm^{-1} in ZrG; 1245, 1336 cm^{-1} in Gly) and the deformation mode of $\delta_{\text{–NH}}$ (1560 cm^{-1} both in ZrG and Gly) suggested the existence of glyphosate molecules in the ZrG crystal layers. Compared to glyphosate, $\nu_{\text{P=O}}$ (1269 cm^{-1} in Gly) and $\nu_{\text{P–OH}}$ (916 cm^{-1} in Gly) disappeared in ZrG, while $\nu_{\text{P–O–Zr}}$ (996, 1072, 1155 cm^{-1} in ZrG) appeared on the contrary. Thus it could be confirmed that glyphosate was immobilized in inorganic veneer sheets by the formation of P–O–Zr bonds using all the three oxygen atoms of the O=P(OH)$_2$– groups. $\nu_{\text{C–OH(COOH)}}$, $\nu_{\text{C=O}}$ (1727 cm^{-1} in ZrG; 1733 cm^{-1} in Gly), $\delta_{\text{–NH}}$ and $\nu_{\text{–NH}}$ (1484 cm^{-1} in Gly) were

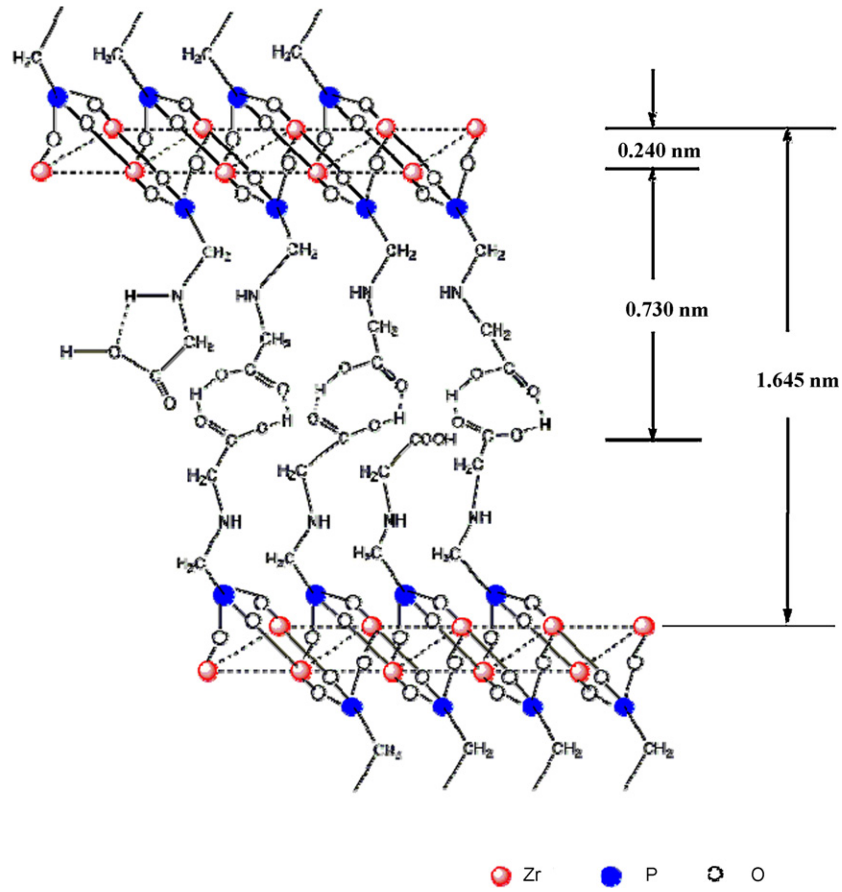

Fig. 2. Laminar crystal structure of ZrG.

weakened or even disappeared after glyphosate intercalation, which suggested the restriction of the motions of C–OH (–COOH), C=O and –NH, induced by the interlayer or intramolecular hydrogen bonds between these groups.

The XRD and FTIR results both confirmed the network of hydrogen bonds structure in the crystal layers. Based on the above characterization results and the molecular composition reported in the literature ($Zr(O_3PCH_2NHCH_2COOH)_2{\cdot}0.5H_2O$) [18], the laminar structure and the hydrogen bonds network of the as-synthesized ZrG were illustrated in Fig. 2.

3.2. *Characterizations of the hybrid membranes*

The successful sulfonation of PEEK was verified by FTIR spectra (DS 41.8%, Fig. 3). The absorptions at 1024, 1082, 1252 cm^{-1} were attributed to the sulfur–oxygen (O=S=O) vibration, and those at 1495 and 1475 cm^{-1} were attributed to the C–C aromatic vibration [19,25]. The typical absorption bands of ZrG were also shown in the figure but in the spectra of the hybrid membranes the bands were overlapped by those of SPEEK. The thermogram curves of ZrG and membranes were shown in Fig. 4. For ZrG, the weight loss below 200 °C was due to the vaporization of the crystal water, and the weight loss in the temperature range of 200–300 °C and thereafter indicated the simultaneous decomposition of the interlayer organic chains and the chemical transformation of ZrG to zirconium pyrophosphate (ZrP_2O_7), respectively [18,23]. The weight loss of ZrG induced by the interlayer organic chains was inhibited when ZrG was incorporated into the hybrid membranes. The composite membrane showed a comparable thermal stability to the pristine membrane.

3.3. *Water uptake and swelling property*

The water uptake and swelling of the pristine SPEEK membrane at 25 °C were found to be 33.3% and 28.0%, respectively (Table 1). After incorporation of ZrG particles, the water uptake decreased by 3–4% in the doping range of 4–16 wt%. This slight decrease was due to the less swelling nature of ZrG than SPEEK, but the limited doping amount and the water retention capacity of the carboxyl groups would impede further reduction in hydrophilicity. The relatively low water uptake of the SPEEK/ZrG hybrid membranes decreased

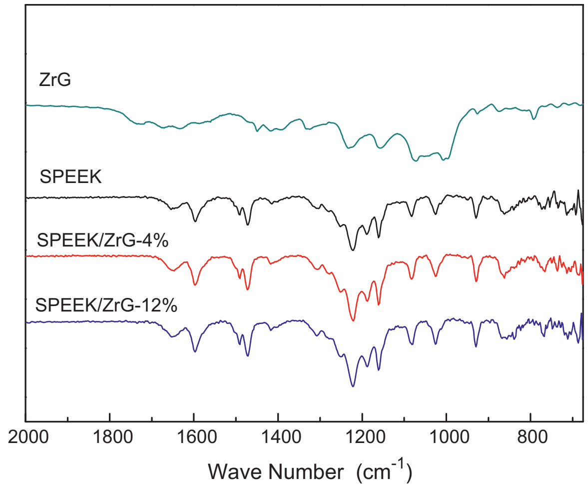

Fig. 3. FTIR spectra of the pristine SPEEK and SPEEK/ZrG hybrid membranes.

Table 1
Data of the water uptake, swelling, methanol permeability and selectivity at 25 °C of the pristine SPEEK and SPEEK/ZrG hybrid membranes.

Membrane	Water uptake (%)	Swelling (%)	Methanol permeability ($\times 10^{-7}$ cm^2 s^{-1})	Conductivity ($\times 10^{-2}$ S cm^{-1})	Selectivity ($\times 10^{5}$ S s cm^{-3})
SPEEK	33.3	28.0	1.88	5.16	2.74
SPEEK/ZrG-4%	29.9	22.4	1.63	5.84	3.58
SPEEK/ZrG-8%	29.3	22.0	1.49	6.74	4.52
SPEEK/ZrG-12%	29.2	21.4	1.43	6.74	4.71
SPEEK/ZrG-16%	29.1	17.2	1.61	7.13	4.43

the swelling degree, hence might improve the hydrolytic stability of the membranes and be advantageous for the methanol barrier property.

3.4. Methanol permeability

The methanol permeability decreased with the content of ZrG (Table 1). In the case of the membrane containing 12 wt% ZrG, the methanol permeability was reduced to 1.43×10^{-7} cm^2 s^{-1}, about 25% lower than the pristine SPEEK membrane. Compared with the commonly used perfluorinated sulfonic acid membranes (e.g. 6.08×10^{-6} cm^2 s^{-1} for pure Nafion® [5], 2.36×10^{-6} cm^2 s^{-1} for Nafion® 115 [21]), the pristine SPEEK membrane exhibited much lower methanol permeability due to its less pronounced phase separation between the hydrophilic and hydrophobic domains than that occurred in Nafion®. This reduced phase separation led to narrowed ionic channels which were less connected and more branched with more dead-end "pockets" [26]. These characteristics would inhibit the mobility of the methanol molecules and lead to a lower fuel crossover through the membrane. After the incorporation of ZrG, the diffusion pathways were further prolonged and became more tortured, and thus the methanol permeability was further reduced. When the ZrG loading increased to 16 wt%, the less uniform dispersion of ZrG in the hybrid membrane exerted an unfavorable effect on methanol rejecting ability, the permeability increased slightly to 1.61×10^{-7} cm^2 s^{-1}, but was still lower than that of the pristine one by 14%.

3.5. Proton conductivity and selectivity

Proton conductivity was the crucial parameter for the evaluation of the fuel cell membranes. The conductivity of the as-prepared membranes with various ZrG contents was first measured in plane by the two-point-probe method at 25 °C (Fig. 5(a)). The pristine SPEEK membrane showed a conductivity of 0.0516 S cm^{-1}, which was considered to be acceptable for low temperature DMFC applications [27]. As discussed before, the incorporation of non-proton-conducting inorganic fillers often leads to a reduction in proton conductivity, and the reduction will be even more severe with increasing content. However, in the current study, the proton conductivity of the hybrid membranes increased with increasing ZrG content. It was speculated that the increase in conductivity after incorporation of ZrG arose from the additional acid groups grafted on the inorganic crystals as well as the favorable regular interlaminar proton-conducting channels formed in the lamellar crystals. The proton conduction was recognized to be governed by two kinds of mechanisms, i.e. the vehicle mechanism (the migration of hydrated protons, e.g. $H_5O_2^+$, $H_9O_4^+$, etc. [28]) and

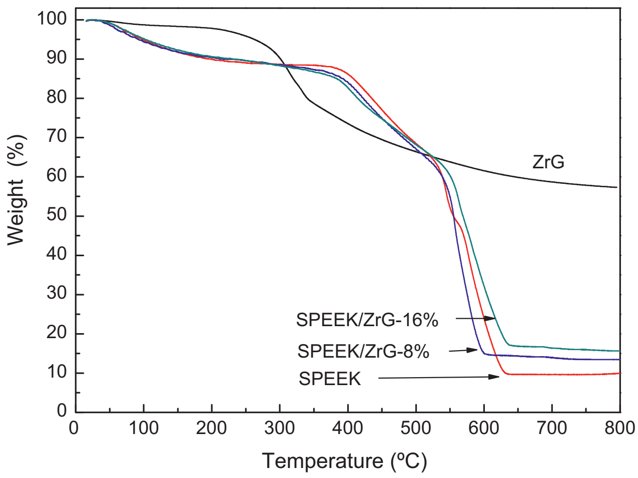

Fig. 4. TGA curves of the pristine SPEEK and SPEEK/ZrG hybrid membranes.

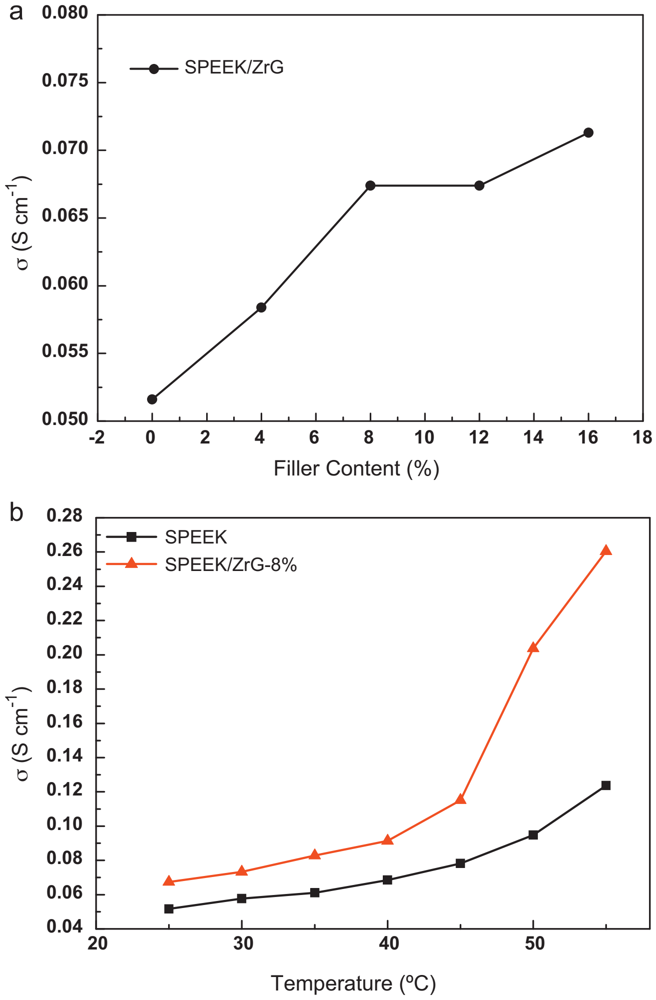

Fig. 5. Proton conductivity of the pristine SPEEK and SPEEK/ZrG hybrid membranes with the ZrG content (25 °C) (a) and the temperature (b).

the Grotthuss mechanism (hopping among water molecules or functional groups by the continuous formation and breaking of hydrogen bonds [29,30]). The non-permeable inorganic fillers disturbed or even blocked the ionic channels for the transfer of the water-solvated protons; and furthermore, the –SO_3H groups in the hydrophilic channels, which served as the proton-conducting sites, may also be separated after the filler incorporation. Herein, the IEC of SPEEK was measured to be 1.3 mmol g^{-1} and the –COOH groups content 4.6 mmol g^{-1} (ZrG). The acid conducting sites were locally enriched in the inorganic domains which would facilitate the proton transfer through the membrane by hopping mechanism. It could also be hypothesized that the preferable structure of the ZrG crystal layers with an appropriate *d*-spacing allowed a favorable organization of the carboxyl group network, thus providing additionally new and efficient proton-conducting channels between the crystal layers. The abundant acid groups in the membrane and the proton-conducting channels in the crystal layers contributed to the enhanced proton conductivity. In addition, the existence of the abundant carboxyl groups both on the ZrG crystal surface and between the interlayers enhanced the compatibility of the inorganic fillers with the organic matrix without destroying the conducting domains of the SPEEK matrix. Compared with the pristine SPEEK membrane, the proton conduction of the hybrid membrane was increased by 13% at the ZrG content of 4 wt%, and further increased by 38% up to 0.0713 S cm^{-1} at the ZrG content of 16 wt%, which was comparable to Nafion® membranes [31].

Proton conductivity under 100% relative humidity at elevated temperatures (from 25 °C to 55 °C) was measured and depicted in Fig. 5(b). In the temperature range tested, the proton conductivity of both the pristine and the hybrid membranes increased with temperature due to the enhanced proton transfer kinetics [2]. The hybrid membranes showed a higher proton-conducting ability than the pristine one in the experimental temperature range. The benefit of the addition of ZrG for proton conductivity was reflected more notably when the temperature increased above 45 °C. Similar results had been found in case of incorporation of solid acid fillers [10]. The association and dissociation of –COOH groups were facilitated at higher temperatures, thus more delocalized protons were generated [32]. The –SO_3H groups were completely ionized at room temperature so long as there was enough water present [33]. Owing to the high acid group (–COOH) density in ZrG, which was much higher than that of –SO_3H groups in the SPEEK matrix, the proton conductivity of the hybrid membrane was promoted more obviously at higher temperatures. In addition, owing to the water retention capacity of –COOH groups induced by its large hydration energy and strong hydrogen bonds [34], the water available for proton transfer by either the vehicle mechanism or hopping mechanism would be maintained even at elevated temperatures.

The selectivity (the ratio of the proton conductivity to the methanol permeability) of the membrane was commonly used as a guideline for the evaluation of the comprehensive performance of membranes [1,35,36]. The selectivity parameters for the as-prepared membranes were calculated and listed in Table 1. As both the proton conductivity and the methanol barrier property were enhanced after the addition of the lamellar-structured ZrG, the selectivity was increased. The SPEEK/ZrG-12 membrane with a ZrG content of 12 wt% exhibited the highest selectivity of 4.71×10^5 S s cm^{-3} at 25 °C, which was 72% higher than the pristine membrane.

4. Conclusion

The lamellar crystals of ZrG with interlayer spacing ~1.645 nm and organic pendants terminated by –COOH groups were synthesized and incorporated into SPEEK matrices to prepare hybrid membranes with enhanced methanol barrier property without scarifying proton-conducting ability. New proton-conducting channels were formed inside the interlayers by the network of the proton-conducting groups. Proton conductivity was enhanced with increasing ZrG content and temperature. Meanwhile, the pathways for methanol diffusion were prolonged and tortured, leading to a reduction of methanol crossover. Overall, the SPEEK/ZrG membranes exhibited desirable comprehensive performance, showing promising prospects for application in DMFCs. The introduction of layered proton conductors in pristine proton conductive polymer membranes may provide an alternative strategy for the development of PEMs by constructing additional proton-conducting channels.

Acknowledgements

We gratefully acknowledge financial support from the National Nature Science Foundation of China (No. 20776101), the Programme of Introducing Talents of Discipline to Universities (No. B06006), the Program for Changjiang Scholars and Innovative Research Team in University from the Ministry of Education of China and the Project-sponsored by SRF for ROCS, State Education Ministry and the National Basic Research Program of China (No. 2008CB617502). We gratefully thank Professor Yuxin Wang for his help in the synthesis of SPEEK.

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