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Review on Modification of Sulfonated Poly (-ether-ether-ketone) Membranes Used as Proton Exchange Membranes

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The proton exchange membrane fuel cell (PEMFC) is a type of modern power, but the traditional proton exchange membranes (PEM) of PEMFC are limited by high methanol permeability and water uptake. Poly-ether-ether-ketone (PEEK) is a widely used thermoplastic with good cost-effective property. Sulfonated poly (-ether-ether-ketone) (SPEEK) has high electric conductivity and low methanol permeability, as well as comprehensive property, which is expected to be used as PEMs. However, the proton exchange ability, methanol resistance, mechanical property and thermal stability of SPEEK are closely related to the degree of sulfonation (DS) of SPEEK membranes. Additionally, the proton conductivity, methanol permeability, and stability of SPEEK membranes applied in various conditions need to be further improved. In this paper, the research into modification of SPEEK membranes made by SPEEK and other polymers, inorganic materials are introduced. The properties and modification situation of the SPEEK and the composite membranes, as well as the advantages and disadvantages of membranes prepared by different materials are summarized. From the results we know that, the methanol permeability of SPEEK/PES-C membranes is within the order of magnitude, $10^{-7}cm^2/s$. The proton conductivity of the SPPESK/SPEEK blend membrane reaches 0.212 S cm^{-1} at 80 °C. The cross-linked SPEEK membranes have raised thermal and dimensional stability. The non-solvent caused aggregation of the SPEEK ionomers. The proton conductivity of SPEEK/50%BMIMPF$_6$/4.6PA membrane maintains stable as 2.0×10^{-2}S cm^{-1} after 600 h at 160 °C. Incorporation of aligned CNT into SPEEK increases the proton conductivity and reduces the methanol permeability of the composite membranes. The PANI improves the hydrothermal stability. More proton transfer sites lead to a more compact structure in the composite membranes. According to the results, the proton exchange capacity, water uptake, and conductivity of the SPEEK membranes are closely related to the structure, stability, mechanical and electrochemical property and methanol permeation of the PEMFC. The modification of SPEEK membranes will improve their applications in aviation, military and other industries. Some proposals for further research are put forward.

Keywords: sulfonated poly (-ether-ether-ketone), proton exchange membrane, modification.

1. INTRODUCTION

The renewable and clean energy is one of the pressing international demands in the world [1].

As a kind of modern power of dynamo-electric vehicle, proton exchange membrane fuel cell (PEMFC) has high efficiency and energy density, it is harmless to environment [2 – 3]. As a barrier to the fuel gas between the electrodes, proton exchange membrane (PEM) plays key role in transferring protons from the anode to cathode of the PEMFC. The membranes traditionally used in PEMFC are perfluorosulfonic polymers such as Dupont Nafion, which have high proton exchange ability and good chemical stability. However, some disadvantages limited their further application, their water uptake, methanol permeability and cost are quite high at certain conditions [4]. So many research works have been focused on developing the PEM with more comprehensive performance. Poly-ether-ether-ketone (PEEK) is a kind of thermoplastic with good cost-effective property [5 – 7]. It is widely used in space-flight, petroleum, chemical and medical industrial fields because of its heat and corrosion resistant, outstanding toughness and machining property [8 – 11]. SPEEK has high electric conductivity and low methanol permeability, as well as high ion exchange capacity (IEC), good mechanical property and stability, which is expected to be used as PEM to replace the Nafion materials [12 – 15]. But the main properties of the SPEEK depend on the DS, preparation process of SPEEK membranes. Besides, demands from various areas need higher quality SPEEK membranes. This paper introduces the modification of SPEEK membranes.

2. MODIFICATION OF SPEEK MEMBRANES

The proton exchange ability, methanol resistance, mechanical property and thermal stability of SPEEK are closely related to the DS [13, 16 – 22]. The membranes with low DS are methanol and swelling resistant but have poor proton exchange abilities [15]. The membranes, with high DS, have high proton exchange and water uptake ability, but the methanol and swelling resistance decrease [14]. Moreover, The SPEEK membranes used in different environment, such as various temperature and humid conditions, should possess improved comprehensive properties. So the SPEEK membranes need to be modified to enhance the proton conductivity, methanol resistance, thermal, dimensional and mechanical stability. Composite membranes of SPEEK modified with polymers are common technology for improving the mechanical property, water uptake, and the stability and selectivity of

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the membranes in high temperature environment. Additionally, in order to achieve acceptable proton conductivity, high degree of functionalization is required, but the excessive water swelling of SPEEK would weaken the methanol barrier ability and mechanical property [23]. Developing organic-inorganic composite membranes is a feasible and effective way to solve the above problems. The SPEEK membranes can be modified by polymers and inorganic fillers to achieve composite membranes with improved properties.

3. MODIFICATION OF SPEEK MEMBRANES WITH POLYMERS

A variety of modification approaches such as cross-linking and blending have been explored to prepare efficient membranes based on SPEEK [24].

3.1. The blend membranes of SPEEK with polymers

The blend membranes of SPEEK with polymers will further improve swelling, methanol permeability, and enhance the proton conductivity of SPEEK membranes, and meet the demands of service life and stability for the membranes in various temperature and humid conditions [25].

The high proton conductivity of the membranes need high DS and service ability at elevated temperature, but the SPEEK membrane with fairly high DS can swell excessively and even dissolve at high temperature. For this reason, phenolphthalein poly (-ether sulfone)(PES-C) and sulfonated phenolphthalein poly (-ether sulfone)(SPES-C, DS = 53·7 %) were blended into SPEEK polymer to prepare SPEEK/PES-C and SPEEK/SPES-C composite membranes by GAO Qijun et al. [26]. The results revealed that the two blended polymers show good miscibility. Both PES-C and SPES-C could decrease the swelling degree and methanol permeability effectively. Pure SPEEK membrane dissolved completely at 75 °C, the swelling degree of SPEEK/PES-C (30 %) and SPEEK/SPES-C (30 %) were 22.5 % and 26.32 % at 80 °C, respectively. From room temperature to 80 °C, the methanol permeability of blend membranes were within the order of magnitude, $10^{-7}cm^2/s$, which was about one order of magnitude lower than that of Nafion®115. Under 100 % RH, the proton conductivity of blend membranes with 20 wt.% PES-C exceeded that of Nafion®115 at above 90 °C, the proton conductivity of blend membranes with 30 wt.% SPES-C reached 0.11 S cm^{-1}, comparable to Nafion®115 at 110 °C.

The sulfonated poly (phthalazinone ether sulfone ketone) (SPPESK) with low swelling rate and the SPEEK with good water uptake were used to prepare SPPESK/SPEEK blend proton exchange membrane by Du Liguang et al. [27]. The results showed that the water uptake and swelling rate of the SPPESK/SPEEK blend membrane were 101 % and 34 % at 80 °C, respectively. The methanol swelling rate and the proton conductivity of the blend membrane was 20 % and 0.212 S cm^{-1} at 80 °C. The flexibility of the blend membrane was better than that of SPPESK. The SPEEK improved the increase of tensile strain, from 16.48 % to 30.43 %.

SPEEK and fluorinated polymer based blends for low temperature (< 80 °C) fuel cell applications were prepared by Inan Tülay Y. et al. [28]. The results showed that the water uptake and proton conductivity values decreased with the addition of fluorinated polymers (PVDF, PVDF-HFP) as expected, but proton conductivity values were still comparable to that of Nafion 117 membrane. The fluorinated polymers improved the chemical degradation of the blend membranes, yet addition of the PVDF-HFP to the SPEEK70 caused phase separations. The methanol permeability of SPEEK70/PVDF blend membrane (3.13×10^{-7} cm^2/s) was much lower than Nafion 117 (1.21×10^{-6} cm^2/s). Hydrogen and oxygen permeability values were 1/10 and 1/5 of the Nafion, respectively.

The results of preparation of blend membranes of SPEEK show that the PES-C and SPES-C appear good miscibility with SPEEK. The swelling and methanol permeability are reduced effectively by adding the PES-C and SPES-C into SPEEK. The blended membranes of SPPESK and SPEEK can bear methanol with higher concentration, which has better proton conductivity. The compatibility between PVDF-HFP and SPEEK is quite good. The chemical degradation and methanol permeability of the blended membranes are promoted by the PVDF and PVDF-HFP.

3.2. The cross-linked membranes by EB irradiation of SPEEK with polymers

Presently, the radiation-induced cross-linking method utilizing electron beam (EB) has been widely used for polymeric material processing due to their inherent advantages over UV and thermal curing methods. The radiation cross-linking strategy using a cross-linker into SPEEK based membranes is a simple and efficient way, to increase thermal and dimensional stability, mechanical properties of the membranes, and simultaneously, to reduce the methanol permeability and maintain proton conductivity [29]. Song Ju-Myung et al. prepared cross-linked SPEEK membranes by the radiation cross-linking of SPEEK with various cross-linkers, such as polyester acrylate, trimethyol propane triacrylate (TMPTA), 1,6-hexandial diacrylate (HDDA), and 2-(2-ethoxy-ethoxy)ethyl acrylate (EOEOA). They found that the cross-linked membranes have higher cluster *Tg* than Nafion 117 membrane, which indicated that the cross-linked membranes could be more useful than Nafion 117 membrane in high temperature fuel cell. The SAXS data showed that the used cross-linker did not affect the ionic domain morphology in the membranes. The proton conductivity of all the membranes exceeded 10^{-2} S cm^{-1}. The cross-linked SPEEK membranes, with better thermal and dimensional stability, would possibly improve the performance of PEMFC, especially, at high temperature (90 °C).

In order to mitigate problems associated with dimensional stability, mechanical strength, and methanol crossover, the 1,6-bis (4- vinylphenyl) hexane (BVPH), an unhydrolyzable cross-linker, was prepared and used to cross-link SPEEK membranes by EB irradiation by Han Sanghee et al. at room temperature [30]. Compared to the pristine SPEEK membrane, the cross-linked membranes exhibited significantly improved dimensional and chemical stability, and mechanical strength. The cross-linking of SPEEK with BVPH slightly reduced the proton conductivity of the membranes, but significantly reduced the methanol permeability

Cross-linked SPEEK membranes were prepared using an EB-irradiation cross-linking method with various contents of cross-linker mixture (1,4-butanediol divinyl ether (BDVE)/triallyl isocyanurate (TAIC), 9/1 wt. ratio) and applied as PEM for fuel cell application by Song Ju-Myung et al. [31]. They found that the degree of cross-linking and the chemical stability of the EB-cross-linked SPEEK membranes were enhanced by the increase of the BDVE/TAIC cross-linker content from gel fraction results. Nevertheless the water uptake, IEC, and proton conductivity of the cross-linked membranes decreased with the content increase of the cross-linker mixture. The DMA and SAXS data indicated that the EB-cross-linked SPEEK membrane have well-developed ionic aggregation in the cluster regions. In addition, the current density of the cross-linked membranes was higher than 1198 mA/cm^2 at a 0.4 voltage (V) under fully hydrated condition at 80 °C with a 1.5 bar backpressure from a MEA cell performance test. Compared to the pristine SPEEK membrane, the cross-linked membranes achieved by EB irradiation, exhibit significantly improved dimensional, thermal and chemical stability, and mechanical strength. The cross-linking process slightly decreases the proton conductivity but significantly reduce the methanol permeability of the SPEEK membranes. So, it can be seen that the cross-linking process is very effective way for improving the properties of the SPEEK membranes, and the membranes could be more useful than Nafion 117 in high temperature fuel cell.

3.3. The modification of SPEEK membranes with other polymers

A series of semi-interpenetrated polymer network (semi-IPN) combining fluorinated hexane network and linear SPEEK (L-SPEEK) were obtained by varying the SPEEK content from 50 to 80 wt.% by Linda Chikha et al. [32]. These semi-IPNs displayed good thermal stability and moderated water uptake swelling. Their chemical stabilities in the Fenton reagent were estimated to be 10 times higher than that of the L-SPEEK.

PTFE has good compatibility with Nafion resin because of their similar chain structures. A composite membrane based on SPEEK and porous PTFE was prepared by Bi Cheng et al. [33]. The PTFE substrate was hydrophilically pretreated by naphthalene sodium solution. The results indicated that the SPEEK can impregnate into treated PTFE substrate (trPTFE) easily. The mechanical property of SPEEK/trPTFE membrane has advantages over pristine SPEEK membrane. Thinner composite membrane would be applied in single cell due to the reinforced effect of trPTFE on substrate.

Liu D. et al. prepared long cross-linked composite membranes, in which, the SPEEK particles were dispersed in a non-proton conductive polymeric matrix, a cross-linked poly(dimethyl siloxane) (PDMS) [34]. Experimental results indicated that the long SPEEK chains improved the conductivity of the membrane, water uptake, and dimensional stability, and the chains also caused the increase of the methanol permeation. The membranes displayed anisotropic swelling behavior in water which then promotes the enhancing of the mechanical stability in humidity cycling.

PEEK and SPEEK were synthesized via nucleophilic aromatic substitution reaction, then the bromomethylated poly(ether ether ketone) (PEEK-Br) was prepared and reacted with 2-benzimidazolethiol to obtain the benzimidazole grafted poly(ether ether ketone) (PEEK-BI) by Li Hongtao et al. [35]. The results showed that the composite membranes exhibit better mechanical properties as well as reduced water uptake and methanol permeability than the pristine SPEEK membrane. The increased oxidative stability and selectivity indicated that the composite membranes are promising to be used as PEM.

Polymer electrolyte membranes (PEMs) were developed for DMFC applications, based on SPEEK and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) filled with Cloisite 30B (C 30B) as a solid hydrophilic proton conductor [36]. PEMs were characterized using liquid uptake, oxidative stability, TGA, XRD, SEM, AFM and impedance analysis. The single cell DMFC performance revealed that the optimized PEM showed an open circuit voltage (OCV) of 0.79 V and a maximum power density value of 55 $mW\,cm^{-2}$ with a proton conductivity value in the range of 10^{-2} $S\,cm^{-1}$. The methanol permeability and selectivity ratio of the optimized membrane were 1.35×10^{-7} $cm^2\ s^{-1}$ and 9.63×10^4 $S\,s\,cm^{-3}$, respectively. As a result fabricated membranes could be seen as promising PEMs for DMFC applications.

Membrane casting solution of SPEEK dispersed in the mixture of solvent dimethyl formamide (DMF) and non-solvent (tetrachloroethylene or paraxylene) was used to prepare SPEEK electrolyte membranes by ZHANG Li-Juan et al. [37]. The proton conductivity and water permeability were increased by around 50 % – 60 % and 30 % respectively, compared to the membrane casting from SPEEK/DMF solution. The non-solvent caused aggregation of the SPEEK ionomers, which then affected the structure and performance of the resultant membranes.

Reviewing the properties of composite membranes of SPEEK, we can find that the semi-IPNs composed of fluorinated hexane network and L-SPEEK display good thermal stability and moderated water uptake and swelling. The membranes made of trPTFE and PEEK show excellent mechanical properties. The long cross-linked chains formed by suspension SPEEK particles improve the proton conductivity, water uptake and dimensional stability of the membranes. The composite membranes of PEEK-Br and PEEK-BI exhibit greatly improved mechanical properties, water uptake and methanol permeability, the oxidative stability and selectivity increased as well. The introduction of PVDF-HFP/C 30B improves the dimensional, thermal and oxidative stabilities of PEMs. The obtained methanol permeabilities of the membranes are lower than that of Nafion® 117. Compared to the SPEEK/DMF membranes, the non-solvent used in the SPEEK membranes increased the proton conductivity and water permeability by around

50 % – 60 % and 30 % respectively, but the non-solvent caused aggregation of the SPEEK ionomers.

4. MODIFICATION OF SPEEK MEMBRANES WITH INORGANIC MATERIALS

For practical use, PEM must possess excellent mechanical properties and high proton conductivity simultaneously [38]. The organic–inorganic composite membranes would combine the remarkable mechanical property of the polymer matrix with the high intrinsic conductivities of the inorganic additives. At the same time, the inorganic components can suppress excessive water swelling and methanol crossover, while improving mechanical and thermal stabilities of the composites [39].

4.1. Modification of SPEEK membranes with SiO_2 materials

Silicon dioxide (SiO_2) is widely used for composite membranes due to its good mechanical properties and water retention [23]. A series of organic/inorganic hybrid materials based on SPEEK/SiO_2 were used to produce electrolytic membranes for DMFC.

XU Dan et al. prepared SPEEK/SiO_2 composite membranes based on sulfonated silica/ SPEEK by means of sol-gel method so as to gain high conductivity and reasonable methanol permeability [40]. The sulfonated silica was generated in situ via the hydrolysis of sulfonated 3-anminopropyl triethoxysilane(KH550). The membrane with silica mass fraction of 5 % exhibited conductivity of 0.187 S cm^{-1} and methanol coefficient of $9.72 \times 10^{-7} cm^2/s$ at 80 °C. The composite membranes showed better conductivity and selectivity which are promising for DMFC application.

Vijay Shankar Rangasamy et al. investigated the effect of the silica functionalisation route on the thermal, mechanical and structural properties of SPEEK-silica composite membranes [41]. They compared two different methods – direct sulfonation and co-condensation (sol-gel) to add sulfonic acid groups to silica nanoparticles, which were used as fillers in SPEEK membranes. The DS of the cast membranes determined by ^{1}H NMR ranged from 40 % to 86 %. TGA-DSC measurement showed higher desulfonation temperatures for the composite membranes, indicating better thermal stability compared to pure SPEEK membranes. DMA results showed that the sol-gel membranes were mechanically more stable within a wider operational temperature range than the directly sulfonated and pristine SPEEK membranes. Water uptake of the membranes increased with silica content, indicating the formation of additional water-mediated pathways for proton conduction.

Du Lin investigated the sulfonation conditions and the swelling resistance of the SPEEK with various DS, to determine the suitable scope of DS in SPEEK for inorganic modification [39]. The silica sulfuric acid (SSA) and the superacid tin oxide ($SSnO_2$) nanoparticles were synthesized, and the SPEEK/SSA and SPEEK/$SSnO_2$ composite membranes were characterized respectively. The results showed that high-DS SPEEK has poor swelling resistance and the SPEEK with DS within 50 % – 60 % has good mechanical stability in water. The SPEEK/SSA composite membrane doped with 5 wt.% SSA nanoparticles showed the best performance at 80 °C, the water uptake of the membrane was 56.4 %, conductivity was 0.13 S cm^{-1}, which is 18.6 % higher than that of SPEEK membrane. The composite membranes also exhibited higher water uptake and conductivity than the SPEEK membrane. When the relative humidity (RH) was 40 % and 80 % at 80 °C, the conductivity of SPEEK-5SSA was 166.4 % and 48.5 %, higher than the pristine SPEEK membrane, respectively. The conductivity and elastic modulus increased, whereas the swelling ratio decreased with the increase of the $SSnO_2$ content.

Among a variety of fillers, polyhedral oligomeric silsesquioxane (POSS) has drawn a considerable attention in last few years. A typical POSS macromere is a cage-like hybrid molecule of silicon and oxygen, ranging from approximately 1 – 3 nm in size [42]. They have chemical composition of $RSiO_{1.5}$, similar to both silica (SiO_2) and silicons $(R_2SiO)_n$. Conceptually, POSS itself may be thought of as the smallest particle of silica. POSS is rigid and inert like inorganic filler, and can molecularly dissolve in a polymer matrix. Novel hybrid composite membranes were prepared by blending poly (-ethylene glycol) functionalized polyhedral oligomeric silsesquioxane [PPOSS], as nanofiller in varying concentration ranging from 1 to 5 % (w/w), into SPEEK by Deeksha Gupta et al. The effect of incorporation of PPOSS into SPEEK matrix was investigated in terms of thermomechanical and morphological properties, water uptake and proton conductivity of SPEEK. All the composite membranes were thermally and mechanically stable up to 250 °C. Transmission electron microscopy (TEM) revealed the small particle size (∼100 nm, 2 wt.%) of PPOSS dispersed in SPEEK membranes, and agglomeration of PPOSS (∼300 nm) was observed at higher loading. The proton conductivity was found to be dependent on the morphology and was independent of the amount of water present in the membranes. The highest proton conductivity (0.047 S cm^{-1} compared 0.034 S cm^{-1} for net SPEEK) gained at 100 °C and 100 % RH.

Summary of properties of composite membranes of SPEEK containing SiO_2 implying that the interaction between the functional groups of silica and the sulfonic groups of polymer can influence the water uptake, swelling and conductivity of the membranes. The IEC, water uptake and swelling measurements highlight that the silica contributes to reduce the swelling through interactions between sulphonic and aminic groups. The composite membranes prepared by reduced SPEEK and isocyanate propyl trioxethyl silane have lower methanol permeability and similar proton conductivity than Nafion membrane, the thermal and dimensional stability increase with the increase of SiO_2 in the membranes. The SiO_2 is helpful for improving the form of compact structure and then raise the mechanical stability and the swelling resistance. The SiO_2/SPEEK membranes show improved conductivity and better selectivity. The SPEEK/SSA and SPEEK/$SSnO_2$ composite membranes, with DS in the range of 50 % – 60 %, have good mechanical stability in water. The SPEEK/SSA membranes doped with 5 wt.% SSA show the best performance. The SPEEK-silica composite membranes show better thermal and mechanical stability compared to pure SPEEK membranes within wider operational temperature range. The formation of water-mediated pathways for proton conduction improves the water uptake of the membranes. The incorporation of varying amounts of PPOSS into SPEEK matrix results thermally, mechanically and hydrolytically stable composite membranes with increased proton conductivity. The composite membranes showed higher water uptake and proton conductivity as compared to that of neat SPEEK membranes. However, agglomeration occurs after certain concentration of PPOSS.

4.2. Modification of SPEEK membranes with CNTs materials

Carbon nanotubes (CNTs) are one of the advanced nanomaterials for fabrication of high-performance polymer composites. Recently, CNTs are used as fillers in SPEEK to overcome the DS dependent problems.

The major risk for using CNTs to modify PEMs in fuel cells is possible short-circuiting due to the excellent electrical conductivity of CNTs. Inspired by the electronic shied effect of silica and the excellent water retention, silica-coated CNTs (SiO_2@CNTs) were successfully prepared by a simple sol-gel process and then used as a new additive in the preparation of SPEEK-based composite membranes by Cui Li et al. [23]. The insulated and hydrophilic silica, coated on the surface of CNTs, not only eliminated the risk of short-circuiting, but also enhanced the interfacial interaction between CNTs and SPEEK, and hence promoted the homogeneous dispersion of CNTs in the SPEEK matrix. Moreover, compared to the pure SPEEK membrane ($3.42 \times 10^{-7} cm^2/s$), the methanol permeability of the SPEEK/SiO_2@CNT composite membrane, with SiO_2@CNT loading of 5 wt.%, exhibited almost one order of magnitude decrease of methanol crossover. While the proton conductivity still remained above 10^{-2} S cm^{-1} at room temperature. The obtained results display the possibility of SPEEK/SiO_2@CNT membranes to be served as high-performance PEMs in direct methanol fuel cells.

Nanohybrid membranes of electrically aligned functionalized carbon nanotube (f CNT) with SPEEK have been successfully prepared by solution casting [43]. Functionalization of CNTs was achieved through a carboxylation and sulfonation route. A constant electric field (500 V cm^{-2}) was applied to align the CNTs in the same direction during the drying process of the membranes. All the membranes were characterized chemically, thermally, and mechanically. The proton conductivity and methanol crossover resistance were evaluated to reveal their potential for direct methanol fuel cell application at temperature of 30 °C – 90 °C.

The results showed that the incorporation of aligned CNT reasonably increases the ion-exchange capacity, water retention, and proton conductivity while it reduced the methanol permeability. The maximum proton conductivity (4.31×10^{-2} S cm^{-1}) was found in the SsCNT-5 nanohybrid PEM with higher methanol crossover resistance. The prepared membranes can be used as electrode material in fuel cells and batteries.

The continuous carbon nanofibers (CCNFs) could be easily blended with SPEEK matrix and uniformly dispersed in an electrolyte polymer membrane. Youbo Di et al. incorporated CCNFs into SPEEK to prepare composite membrane for application in PEMs [38]. The characterization of the composite membranes revealed that, all dense composite membranes have excellent water swelling, high mechanical performance, good proton conductivity, and low methanol permeability. The composite membrane with 0.51 wt.% CCNFs displayed proton conductivity of 0.041 S cm^{-1} at room temperature and was fully hydrated. Moreover, the relative selectivity of the hybrid membrane with 2.52 wt.% CCNFs was 1.5 times higher than that of pure SPEEK membrane. These results showed that the CCNF-supported SPEEK membranes are promising polyelectrolyte membranes for fuel cell applications.

From the above research on modification of SPEEK membranes with CNTs materials, we can find that, the SPEEK/SiO_2@CNT composite membranes possess excellent thermal property and methanol barrier performance, as well as relatively high proton conductivity of the. The incorporation of electrically aligned functionalized CNT increases the ion-exchange capacity, water retention, and proton conductivity while it reduces the methanol permeability of the SPEEK composite membranes. Intermolecular interactions between the components in composite membranes were established. The higher proton conductivity and methanol crossover resistance reveal their potential for direct methanol fuel cell application at the temperature of 30 °C – 90 °C. With the assistance of continuous CCNFs, the obtained CCNF/SPEEK membranes have condensed and uniform structures, as well as good mechanical, thermal, and dimensional stabilities. The water uptake and proton conductivity are improved. The composite membranes exhibit relatively low methanol permeability when the contents of CCNFs are controlled. These CCNF/SPEEK membranes are promising materials for PEMFC applications.

4.3. Modification of SPEEK membranes with other inorganic materials

A recent approach to enhance the proton conductivity is to prepare organic–inorganic composite membranes by incorporating SPEEK and fast proton conductors such as zirconium phosphate sulfophenylenlephosphonate, heteropolyacids, and boron phosphate. The hydrophilic nature and excellent water absorption properties of aluminium phosphate ($AlPO_4$) make it an ideal candidate as molecular sieves for various applications.

Composite membranes of SPEEK with different weight ratios of $AlPO_4$ synthesized by sol-gel were prepared by Vijay Shankar Rangasamy et al. [17]. The prepared $AlPO_4$ was used as inorganic filler to enhance the thermal and mechanical stability and the water retention properties of SPEEK membranes. In that study, PEEK was non-homogeneously sulfonated using concentrated H_2SO_4 at different temperatures (room temperature, 60 °C, and 80 °C) and time durations (5, 7, 48, and 72 h). Depending on the DS, the IEC of the membranes varied from 1.06 to 2.9 meq g^{-1}. The water uptake of the membranes increased with DS. The composite membranes showed better thermal and mechanical stability and swelling behavior than the pure SPEEK membranes, however, the water uptake and proton conductivity of the composite membranes were lower than that of pure SPEEK membranes.

Phosphoric acid (PA) doped imidazolium ionic liquid polymer composite membranes were fabricated by immersing the membranes based on imidazolium ionic liquid and polymers of SPEEK or polyvinylidenefluoride (PVDF) into pure phosphoric acid at room temperature [44]. Imidazolium ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) or 1-butyl-3-methylimidazolium dihydrogenphosphate ($BMIMH_2PO_4$) link phosphoric acid molecules to polymer matrix. SPEEK is suitable to capture imidazolium ionic liquid owing to the strong interaction between imidazolium ionic liquid cations ($BMIM^+$) and sulfonic acid group ($-SO_3^-$). So the composite membranes based on SPEEK show prospects for high temperature PEMs.

Although all the components influenced the conductivity values of these composite membranes, phosphoric acid molecular chains played dominant role in the proton conduction. Proton conductivity of SPEEK/50%$BMIMPF_6$/4.6PA membrane at a level of 3.0×10^{-2} S cm^{-1} was achieved at 160 °C under anhydrous conditions. Although the tensile stress at break decreased from 3.12 MPa to 0.10 MPa when the temperature increased from room temperature to 160 °C, the SPEEK/50%$BMIMPF_6$/4.6PA membrane still possessed stable conductivity of 2.0×10^{-2}S cm^{-1} after remaining more than 600 h at 160 °C.

Ren Suzhen et al. fabricated SPEEK/phosphotungstic acid-polyaniline (SPEEK/HPW-PANI) membranes by in situ polymerization of aniline for the purpose of decreasing the weight loss of HPW in the membranes [45]. They synthesized the SPEEK/HPW hybrid membrane and coated PANI on the membrane surface. The scanning electronic microscopy (SEM) images showed that HPW had good compatibility with SPEEK polymers, and energy dispersive X-ray spectroscopy revealed the successfully doping with HPW and polymerization of PANI. The surface of SPEEK/HPW-PANI became more compact than that of SPEEK/HPW and pure SPEEK, which would reduce the water uptake and swelling property. The proton conductivity of the SPEEK/HPW-PANI-5 composite membrane (0.0915S cm^{-1} at 80 °C) was higher than that of pure SPEEK membrane (0.0687 S cm^{-1} at 80 °C). The thermal stability, for both SPEEK/HPW and SPEEK/HPW-PANI membranes, were higher than the pristine SPEEK membrane. The PANI is a good coating material for SPEEK/HPW hybrid membrane, which improves the hydrothermal stable properties. The SPEEK/HPW PANI shows promise performance for PEMs.

As a strong Bronsted acid, the phosphorus wolframic acid (PWA) has good conductivity. Composite membranes, prepared with PWA and SPEEK, can improve proton conductivity, and maintain methanol permeability simultaneously. Tong Juying et al. doped PWA and Y_2O_3 in SPEEK, with relatively high DS, to raise the methanol permeability of the membranes [21]. They gained PWA/Y_2O_3/SPEEK membranes through reaction of SPEEK with concentrated H_2SO_4 at 60 °C. The results show that the methanol permeation coefficient is as low as 4.353×10^{-7} cm^2/s. However, losing of PWA in water will influence the proton conductivity.

Functionalized titania was used as fillers to modify the SPEEK membrane to improve proton conductivity and methanol barrier property by Yin Yongheng et al. [46]. The functionalized titania sol containing proton conductive carboxylic acid groups or amino acid groups was derived from a facile chelation method using different functional additives. Then the novel SPEEK/carboxylic acid-functionalized titania (SPEEK/TC) and SPEEK/amino acid-functionalized titania (SPEEK/TNC) hybrid membranes were fabricated via in situ sol gel method. The anti-swelling property and thermal stability of hybrid membranes were enhanced owing to the formation of electrostatic force between SPEEK and titania nanoparticles. The hybrid membranes exhibited higher proton conductivity than plain SPEEK membrane because more proton transfer sites were provided by the functionalized titania nanoparticles. Particularly, the proton conductivity of SPEEK/TNC membrane with 15 % filler content reached up to 6.24×10^{-2} S cm^{-1}, which is 3.5 times higher than that of the pure SPEEK membrane. The SPEEK/TNC membranes possess the lowest methanol permeability because the acid-base interaction between sulfonic acid groups in SPEEK and amino groups in functionalized titania leads to a more compact membrane structure.

Recently, strong appear to develop PEM for fuel cell, that can work at high temperature under dry condition, makes the Ionic liquids (ILs) attractive due to their excellent chemical and thermal stability, wide electrochemical windows and temperature liquid range, and good ionic conductivity [47]. Singh Malik et al. prepared composite membranes based on SPEEK (DS 70 % – 72%)/ethylene glycol (EG)/IL by solution casting method, using water: ethanol (50 : 50) mixture as solvent, 1-butyl-3-methyl imidazolium trifluromethanesulfonate ([bmim][OTf]) as aprotic hydrophilic ionic liquid, and IL as ion charge carrier at high temperature(30 °C – 140 °C). The EG was used as a cross-linker to reduce the leaching out of ionic liquid and enhance the mechanical strength of SPEEK membranes. Several membranes were prepared by keeping ratio of SPEEK:EG constant (67 : 33 (wt.%)) and varied the amount of ionic liquid (30, 40, 50, 60 and 70 wt.%). The effect of ionic liquid content on proton conductivity, structural, mechanical, thermal properties was evaluated. The cross-linking of SPEEK was carried out by thermal treatment for 2 h at 80 °C, 100 °C, 120 °C, and 135 °C for 16 h respectively. The results showed that the proton conductivity of all the membranes was in the range of 10^{-3} S cm^{-1}, under 30 °C – 140 °C and anhydrous conditions, the proton conductivity increased when the temperature and amount of ionic liquid were raised. The good compatibility between IL and polymer matrix softed the composite membranes due to the plasticizing effect of IL. These membranes are promising materials for high temperature polymer electrolyte fuel cells.

Reviewing of the modification of SPEEK membranes with other inorganic materials, we know that, the $AlPO_4$ prepared by sol-gel can enhance the thermal and mechanical stability and the water retention properties of

SPEEK membranes. But the water uptake and proton conductivity of the composite membranes are lower than that of pure SPEEK membrane. The water uptake of the membranes depends on the DS. The proton conductivity of the SPEEK/50%BMIMPF$_6$/4.6PA membrane remains stable during 600 h at 160 °C. The tensile stress decreases with the raise of temperature. The PANL layers reduce the weight loss ratio of HPW in the SPEEK/HPW hybrid membranes. The SPEEK/HPW-PANI membranes show higher conductivities, slightly increased thermal stability than the pure SPEEK membrane, and the water uptake and swelling ratio in volume of membranes decrease with increasing the PANL layers. The formation of electrostatic force between SPEEK and titania nanoparticles raises anti-swelling property and thermal stability of hybrid membranes, SPEEK/TC and SPEEK/TNC. More proton transfer sites provided by the functionalized titania nanoparticles improve proton conductivity of the hybrid membranes. The proton conductivity of the composite membranes SPEEK/EG/IL are about 10^{-3} S cm^{-1} under 30 °C – 140 °C at anhydrous conditions. The proton conductivity improves with the increase of temperature and amount of ionic liquid. The plasticizing effect of IL softens the composite membranes. The composite membranes have higher thermal stability and are promising for high temperature polymer electrolyte fuel cells.

5. PROPOSALS FOR FUTURE WORKS

The SPEEK membranes are the key components for the PEMs. The proton exchange capacity, water uptake, and conductivity of the SPEEK membranes are closely related to the structure, stability, mechanical and electrochemical property and methanol permeation of the PEMFC. As one new modern power, the SPEEK membranes, with good comprehensive properties, are highly competitive to replace Nafion membranes, and will be expected to be utilized in aviation, military and other industries. According to the above literatures, the advantages and disadvantages of membranes prepared by different methods are summarized in table1. And the following aspects need to be further investigated:

– break-through the difficulties of achieving PEM suitable for high temperature, humidity, and pressure environment;
– develop the fuel cell with stable properties, and enhance the oxidative and hydrolytic stability of system operation;
– analyze the content relationship of SPEEK and different polymers, so as to improve the main properties of the composite membranes;
– promote the interaction between SPEEK and other polymers to increase their compatibility and decrease phase separation;
– adjust the proper proportion of inorganic matter added in polymer to avoid brittleness and hardness of the membrane;
– raise the affinity of membrane with water, so as to increase the proton conductivity;
– improve the distribution of inorganic particles in the membrane in case they influence the conductivity, the tensile strength, and thermal stability of the composite membrane;
– increase the dimensional stability of the membrane under dry and wet conditions to prevent the internal stress accumulation and decline of performance and life expectancy.
– enhance the strength of the membrane to overcome the fragile, peel, and damage of composite membrane;
– develop thick and dense membrane to improve the methanol resistance;
– reduce the diameter of the inorganic particles to increase the specific surface area, and gain good conductivity;
– research the interface connection between the membrane and the electrode to maintain high proton exchange and low methanol permeability.

Table 1. Advantages and disadvantages of modified membranes

Membranes	Advantages	Disadvantages
Blend membranes	Swelling and permeability reduced effectively, good compatibility	Proton conductivity is content dependent, phase separation
Cross-linked membranes	Significantly improved chemical, thermal and dimensional stability, sharply reduced methanol permeability	Proton conductivity reduced and content dependent
Membranes modified with other polymers	Good thermal, dimensional and oxidative stability, and mechanical property, improved water uptake and methanol permeability	Proton conductivity need to be raised
Membranes modified with SiO_2 materials	Low methanol permeability, increased thermal, dimensional and mechanical stability, raised swelling resistance	Proton conductivity need to be raised
Membranes modified with CNTs materials	High proton conductivity and methanol crossover resistance, good thermal, dimensional and mechanical stability, enhanced intermolecular reaction	Methanol permeability and proton conductivity are content dependent
Membranes modified with other inorganic materials	Good thermal, mechanical stability, high and stable proton conductivity	Water uptake is DS and content dependent

6. CONCLUSIONS

In view of the pressing demand for renewable and clean energy in the world, the PEMFC was developed as a type of the modern power. In order to overcome the shortage of the traditional PEMs of PEMFC, SPEEK with high electric conductivity and low methanol permeability, as well as comprehensive property, was modified and expected to be used as PEMs.

The results of modification of SPEEK membranes with polymers show that, the methanol permeability of blend membranes SPEEK/PES-C are within the order of magnitude, 10^{-7} cm^2/s. The water uptake, swelling rate, and the proton conductivity of the SPPESK/SPEEK blend membrane are 101 %, 34 % and 0.212 S cm^{-1} at 80 °C, respectively. The cross-linked SPEEK membranes have raised thermal and dimensional stability, yet reduced water uptake and methanol permeability than the pristine SPEEK membrane. The high loading of the cross-linker mixtures decrease the properties of the membranes. The non-solvent caused aggregation of the SPEEK ionomers, which then affected the structure and performance of the resultant membranes.

The results of modification of SPEEK membranes with inorganic materials show that, the SPEEK composite membranes, with SiO_2 nanoparticles, indicate better thermal and mechanical stability, within a wider operational temperature range. The SPEEK/SiO_2 membranes exhibit conductivity of 0.187 S cm^{-1} and methanol coefficient of 9.72×10^{-7} cm^2/s at 80 °C. The SPEEK/SSA composite membrane shows water uptake of 56.4 %, at 80 °C. The composite membranes of SPEEK with POSS are thermally and mechanically stable up to 250 °C, yet agglomeration appears. Incorporation of aligned CNT into SPEEK membranes increases the ion-exchange capacity, water retention, and proton conductivity while it reduces the methanol permeability of the composite membranes. The SsCNT-5 composite membrane has the proton conductivity of 4.31×10^{-2} S cm^{-1}, as well as higher methanol crossover resistance. The proton conductivity of SPEEK/50%BMIMPF_6/4.6PA membrane maintains 2.0 x 10^{-2} S cm^{-1} stably after remaining 600 h at 160°C, whereas the tensile stress at break decreased. The PANI improves the hydrothermal stable properties. The methanol permeation coefficient of the composite membranes, prepared with PWA and SPEEK, is as low as 4.353×10^{-7} cm^2/s. More proton transfer sites were provided by the functionalized titania nanoparticles which leads to more compact structure in the composite membranes.

From the above results we know that, the modification of SPEEK membranes displays good thermal stability, improved mechanical and proton conductive properties, and moderated water uptake and swelling compared to the original SPEEK membranes. The further investigation of SPEEK membranes is suggested to optimize the parameters and process of the preparation of SPEEK composite membranes to increase the electric conductivity, efficiency and performance of the fuel cell.

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