Review on Inorganic Materials Modified Sulfonated Poly(ether ether ketone) Membranes---Used as Proton Exchange Membranes

Xiaomin Gao
Institute of Chemical Materials, CAEP, Mianyang, Sichuan, China, 621900

Abstract. As proton conductor and fuel separator, the proton exchange membranes (PEMs) are important electrolyte for the proton exchange membrane fuel cell (PEMFC). The Nafion membranes, used as traditional PEMs, are limited by some disadvantages, so the sulfonated poly(ether ether ketone) (SPEEK) with good comprehensive properties is expected to replace the Nafion. In this paper, the SPEEK composite membranes modified by inorganic materials are summarized. The results show that the SiO$_2$, CNTs and some other inorganic materials are prospective candidates for high-performance SPEEK membranes.

1. Introduction
The high energy density and efficiency of the PEMFC have drawn much attention nowadays [1]. As an important factor, the PEM can affect the performance of PEMFC because it acts as proton conductor and fuel separator [1-2]. The traditionally used commercial PEM membrane, Nafion® membranes are cost and limited by the high methanol permeability [3], so the membrane materials with excellent proton conductivity, chemical stability and low cost are widely investigated [4]. With the advantages as high electric conductivity, good mechanical property and stability, and low methanol permeability, the SPEEK is expected to be the best candidate to replace the Nafion [5-6]. Practically, the main properties of the SPEEK are dependent on the DS, the SPEEK membranes with high DS (about 70%) should be modified to improve their mechanical and dimensional stability. One of the simple and effective approaches is to modify the SPEEK membranes with inorganic or inorganic-organic materials [7]. The inorganic materials with high intrinsic conductivities and the polymer matrix with remarkable mechanical property would improve the mechanical and thermal stabilities of the composites membranes [8].

2. Modification of SPEEK Membranes with Inorganic Materials
The modification of SPEEK membranes by various inorganic materials focus on the silica (SiO$_2$) and carbon nanotubes (CNTs) in literatures. The functionalized silica is effective to form the covalent bond and increase the compatibility of the SPEEK and SiO$_2$ [9-11], the incorporation of electrically aligned functionalized CNT could form the condensed and uniform structures of the composite membranes [1,8,12].

2.1. Modification of SPEEK Membranes with SiO$_2$ Materials
The SPEEK/SiO$_2$ hybrid materials can be used to prepare electrolytic membranes because of the good mechanical properties and water retention [13].

The SPEEK/SiO$_2$ composite membranes, with high conductivity as 0.187 S cm$^{-1}$ and methanol coefficient as 9.72×10$^{-7}$ cm$^2$/s at 80°C, were prepared by XU Dan et al. [9]. The composite
membranes are promising for DMFC application for the high conductivity and reasonable methanol permeability.

Crosslinked organic–inorganic membranes are prepared from hydroxyl-functionalized SPEEK and silica to improve dimensional stability and methanol resistance by Shaoguang Feng et al. The above SPEEK is prepared to get a side chained polymer bearing triethoxysilyl groups. These groups allow the membranes to form a crosslinked network. The obtained membranes with covalent bonds exhibit the minimum methanol permeability coefficient of $7.15 \times 10^{-7}$ cm$^2$ s$^{-1}$, though the proton conductivity is decreased[11].

The SPEEK-silica composite membranes were investigated by Vijay Shankar Rangasamy et al. through two different methods - direct sulfonation and co-condensation (sol-gel) [10]. The silica functional route, the sequence thermal, mechanical and structural properties were characterized. The results showed the higher desulfonation temperatures, the additional water-mediated pathways for proton conduction formed, and the membranes were mechanically more stable.

Summary the modification of the SPEEK/SiO$_2$ composite membranes, we know that the SPEEK/SiO$_2$ composite membranes showed better conductivity and selectivity. The covalent bonds and the formation of the crosslink network, between hydroxyl-functionalized SPEEK and silica are helpful to increase the compatibility. The membranes exhibit much lower methanol swelling ratio and water uptake, yet the proton conductivity decreased. The effect of the silica functional route on the properties of SPEEK-silica composite shows better thermal stability. The water-mediated pathways for proton conduction formed, and the sol-gel membranes exhibit better mechanical stability.

2.2. Modification of SPEEK Membranes with CNTs Materials

The DS dependent problems exerted influence on the main properties of SPEEK, so the CNTs were used as fillers in SPEEK to improve the mechanical property, thermal stability, and proton conductivity [1].

Swati Gahlot et al. prepared nanohybrid membranes with aligned functionalized carbon nanotube (f CNT) and SPEEK by solution casting [12]. The membranes showed increased ion-exchange capacity, water retention, proton conductivity and reduced methanol permeability. The maximum proton conductivity reached $4.31 \times 10^{-2}$ Scm$^{-1}$, the membranes can be used for electrode material for fuel cells and batteries.

Youbo Di et al. dispersed continuous carbon nanofibers (CCNFs) into SPEEK matrix [1]. The higher proton conductivity, better water swelling, mechanical performance, as well as lower methanol permeability exhibited in the result membranes. The proton conductivity as 0.041 S cm$^{-1}$ was gained in the membrane with 0.51 wt% CCNFs, which showed the promising applications for fuel cell.

The electronic shied effect and water retention of silica attracted some attentions presently. In order to overcome the short-circuiting of CNTs while modifying the SPEEK, Li Cui et al. coated silica onto the CNTs, the prepared SiO$_2$@CNTs improved the compatibility of the CNTs and SPEEK, the methanol permeability of the SPEEK/SiO$_2$@CNT composite membrane decreased greatly, while the proton conductivity above $10^{-2}$ Scm$^{-1}$ remained at room temperature, which display the possibility of being served as high-performance PEMs[8].

From the above research on modification of SPEEK membranes with CNTs materials, we find that, the incorporation of CNT increases the ion-exchange capacity, water retention, proton conductivity and methanol crossover resistance, while the methanol permeability reduced. The CCNF/SPEEK membranes have condensed and uniform structures, and better water uptake and proton conductivity. The introduction of silica eliminated the short-cutting of CNTs, which then decreased the methanol permeability of the SPEEK/SiO$_2$@CNT.

2.3. Modification of SPEEK Membranes with Other Inorganic Materials

Some other inorganic materials were adopted to modify the proton conductivity, water uptake, ion-exchange capacity, and swelling behavior of SPEEK membranes.

Three kinds of low-cost oxide ($\text{Al}_2\text{O}_3$, SiO$_2$, and TiO$_2$) were used to modify the SPEEK matrix for vanadium redox flow battery (VRFB) application. The hydrogen bonds' were formed between the SPEEK/nano oxide, which improved the thermal, mechanical, and chemical stabilities of the
SPEEK/nanooxide composite. The tested discharge–capacity of composite membranes were higher than that of the Nafion 117 membrane after 200 cycles. The properties of the SPEEK/nano oxide composite membranes show promising potential for the application in VRFB [14].

The Cloisite15A nanoclay was introduced into the SPEEK to improve the water swelling and methanol permeability in the fuel cells, in which the 2,4,6-triaminopyrimidine(TAP) was used as compatibilizer. The achieved Sp63/2.5Cl/5.0TAP polymer–clay membrane with above properties can be served as a promising alternative PEM [15].

Well optimized SPEEK/AIT were fabricated by SPEEK and the amine-functionalized iron titanate (AIT)nanoparticles, the stabilities and water retention of the composite membrane were improved greatly compared with that of the pure SPEEK matrix. The proton conductivity reached 0.12 S cm⁻¹ and power density reached 204 mWcm⁻² at 80°C, which indicates the potential application in PEMFCs[16].

Analysis of the results of SPEEK composite membranes modified by other inorganic materials, we find that, the hydrogen bonds improved the compatibility between the SPEEK and the nano oxide (Al₂O₃, SiO₂, and TiO₂), which subsequently, increased the stabilities, the energy efficiencies and discharge–capacity retentions of the composite membranes. The introduction of the Cloisite15A improved the swelling and barrier properties of the methanol. The excellent stabilities and water retention of the membranes indicates its potential application in PEMFCs.

3. Advantages and Disadvantages of Different Modification Membranes

According to the above research results, the advantages and disadvantages of SPEEK composite membranes modified by different inorganic materials are summarized in table1.

| Membranes modified with different inorganic materials | Advantages/ Disadvantages |
|-------------------------------------------------------|---------------------------|
| membranes modified with SiO₂ materials                | Better thermal and mechanical stability, improved selectivity, water uptake and compatibility, much lower methanol swelling ratio, yet the proton conductivity need to be further raised. |
| membranes modified with CNTs materials                | Uniform and condensed structures, enhanced interfacial interaction and the homogeneous dispersion, the ion-exchange capacity, water retention, proton conductivity and methanol crossover resistance increased, the methanol permeability is content dependent. |
| membranes modified with other inorganic materials     | Good interfacial compatibility, improved stabilities and more compact membrane structure, lower methanol permeability, the anti-swelling property, water retention, proton conductivity and thermal stability enhanced, yet agglomeration of particles reduced the proton conductivity. |

4. Conclusions

The SPEEK membranes with relatively good comprehensive properties were modified by inorganic materials and expected to be used as PEMs in the modern energy power of PEMFCs. The SiO₂, CNTs and some other inorganic materials are advanced candidates for fabrication of high-performance SPEEK composites membranes.

The silica functional route improved the compatibility, the thermal, mechanical and structural properties and the methanol permeability and selectivity for SPEEK-silica composite membranes, the formed water-mediated pathways increased the proton conduction, which displays the promising for DMFCs application.

The SPEEK composite membranes, modified by CNTs show enhanced interfacial interaction between CNTs and SPEEK, and promoted mechanical performance, ion-exchange capacity, proton conductivity, and water retention, yet the methanol permeability reduced. The CCNF-supported SPEEK membranes are promising for PEMs.
Modification of SPEEK membranes with other inorganic materials show that, the modification of SPEEK membranes with inorganic materials display better thermal and mechanical stability and compact structures, improved methanol permeability, proton conduction compared with that of the pristine SPEEK and Nafion membranes, which are promising for PEMs application, yet the agglomeration and the content depend of the particles on the structures and properties of the composite membranes should be further investigated in detail.

5. References

[1] Youbo Di, Wenjuan Yang, Xiaojie Li, et al. Preparation and characterization of continuous carbon nanofiber-supported SPEEK composite membranes for fuel cell application. RSC Adv., 2014, 4, 52001–52007

[2] Shah Alam, Selangor, Malaysia. The preparation and characterization of sulfonated poly (ether ether ketone) and cellulose acetate(SPEEK-CA) membrane in proton exchange membrane fuel cells (PEMFCs) by UV-crosslink technique. 2012 IEEE Colloquium on Humanities, Science & Engineering Research (CHUSER2012), December 3-4, 2012, Kota Kinabalu, Sabah, Malaysia. 637-641

[3] Xu Liu, Xiaoyu Meng, Chuanming Shi, et al. Facile preparation of well-dispersed GO-SPEEK composite membranes by electrospun for fuel cell applications. Mater. Res. Soc. Symp. Proc. Vol. 1 © 2015 Materials Research Society.

[4] Ju-Myung Song, Junhwa Shin, Joon-Yong Sohn, et al. Preparation and characterization of SPEEK membranes crosslinked by electron beam irradiation. Macromolecular Research, Vol. 19, No. 10, pp1082-1089 (2011)

[5] Monica Pica, Roberto D'Amato, Anna Donnadio, et al. Improving the mechanical stability of proton conducting SPEEK membranes by in situ precipitation of zirconium phosphate phenylphosphonates. RSC Adv., 2016, (6): 36606–36614

[6] Parisa Salarizadeh, Mehran Javanbakht, Saeed Pourmahdian, et al. Influence of amine-functionalized iron titanate as filler for improving conductivity and electrochemical properties of SPEEK nanoporous composite membranes. Chemical Engineering Journal. 2016, (299): 320–331

[7] Mingfeng Song, Xuewei Lu, Zhongfang Li, et al. Compatible ionic crosslinking composite membranes based on SPEEK and PBI for high temperature proton exchange membranes. International Journal of Hydrogen Energy. 2016, (41): 12069-12081

[8] Li Cui, Qing Geng, Chunli Gong, et al. Novel sulfonated poly (ether ether ketone)/silica coated carbon nanotubes high-performance composite membranes for direct methanol fuel cell. Polym. Adv. Technol. 2015, 26: 457-464

[9] XU Dan, WANG Yang, ZHANG Yang, et al. Hybrid membrane with high proton conductivity and selectivity based on SPEEK for direct methanol fuel cells. Chem.Res.Chinese Universities.2010, 26(6): 1031-1034

[10] Vijay Shankar Rangasamy, Savitha Thyumanasundaram, Jean-Pierre Locquet. Sulfonatedpoly(ether ether ketone)-functionalised silica composite membranes for applications in proton exchange membrane fuel cells. Int. J. Nanotechnol. 2014,9/10/11: 971-974

[11] Shaoguang FENG, Yuming Shang, Guoshun Liu, et al. Novel modification method to prepare crosslinked sulfonated poly(ether ether ketone)/silica hybrid membranes for fuel cells. Journal of Power Sources 195(2010): 6450–6458

[12] Swati Gahlot, Vaibhav Kulshrestha. Dramatic improvement in water retention and proton conductivity in electrically aligned functionalized CNT/SPEEK nanohybrid PEM.ACS Appl. Mater. Interfaces 2015, 7: 264–272.

[13] Du Lin. Preparation and characterization of SPEEK proton exchange membranes doped with acidified inorganic particles. Masteral Dissertation. Dalian University of Technology. Tutor: He Gaohong. June 2012

[14] Bibo Yin, Lihong Yu, Bo Jiang, et al. Nano oxides incorporated sulfonated poly(ether ether ketone) membranes with improved selectivity and stability for vanadium redox flow battery. J Solid Electrochem.2016, (20): 1271-1283
[15] Juhana Jaafar, A.F. Ismail, T. Matsuura, K. Nagai. Performance of SPEEK based polymer–nanoclay inorganic membrane for DMFC. Journal of Membrane Science 382 (2011) 202–211

[16] Parisa Salarizadeh, Mehran Javanbakht, Saeed Pourmahdian, et al. Influence of amine-functionalized iron titanate as filler for improving conducting and electrochemical properties of SPEEK nanocomposite membranes. Chemical Engineering Journal. 2016, (299): 320-331