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Sulfonated poly(ether ether ketone): efficient ion-exchange polymer electrolytes for fuel cell applications—a versatile review

Berlina Maria Mahimai,^a Gandhimathi Sivasubramanian,^b Karthikeyan Sekar,^{id}^a Dinakaran Kannaiyan^{id}^c and Paradesi Deivanayagam^{id}^{*a}

Fuel cell technology yields cleaner energy resources for diverse applications such as transport, power stationery, and portable devices. This review focuses on the role of sulfonated poly(ether ether ketone) (SPEEK) based proton conducting electrolyte membranes for fuel cell applications. The key objective of the review is to demonstrate the advantages of SPEEK-based composite membranes over Nafion by blending the SPEEK material with fluorinated polymer, hydrocarbon polymer, carbon-based materials, inorganic nanomaterials, etc. The proton conductivity and ion-exchange capacity of SPEEK polymer with various additives/fillers are highlighted. Since SPEEK polymer is produced in an eco-friendly approach, the composite membranes derived from SPEEK are much more appropriate for both PEMFC and DMFC applications. Herein, the comprised data displayed that the SPEEK-based composite membranes might be urgently considered a potential candidate for fuel cell systems.

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1. Introduction

A fuel cell is one of the vast enabling technologies for future sustainable hydrogen, carbon zero cycles, and circular economy.

In a fuel cell, the chemical energy is converted into electrical energy with less environmental impact.^{1,2} In the past two decades, fuel cell applications are widely in demand in the form of engines, power stationary and portable power sources.³ In the electrochemical reactions of the fuel cell, the fuel is directly oxidized to produce water vapour, heat, and electricity. A variety of fuels such as ethanol, methanol, and hydrogen, are generally used in fuel cell systems. Therefore, electrochemical reactions in the fuel cell are explained as follows: hydrogen passes through the anode has changed into hydrogen ions, while electrons are released, which travel through an external circuit, and finally,

^a Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur-603203, Chengalpattu District, Tamilnadu, India.
E-mail: paradesi77@yahoo.com

^b Department of Physics, SRM Valliammai Engineering College, Kattankulathur-603203, Chengalpattu District, Tamilnadu, India

^c Department of Chemistry, Thiruvalluvar University, Vellore-632115, Tamilnadu, India



Berlina Maria Mahimai

Berlina Maria Mahimai completed her PhD degree in Chemistry from SRM Institute of Science and Technology, Kattankulathur, Tamil Nadu, India. She received her Master's degree in St. Joseph's College, Trichy, India, affiliated to Bharathidasan University in 2018. Her current research is focused on polymer electrolyte membranes doped with inorganic additives for fuel cell applications.



Gandhimathi Sivasubramanian

Gandhimathi Sivasubramanian completed her PhD degree from Anna University, Chennai. She received her Post Graduate degree in Physics from Sarah Tucker College affiliated to Manonmanium Sundaranar University. She is currently working as an Assistant Professor in Department of Physics, SRM Valliammai Engineering College, Kattankulathur, Tamil Nadu, India. She is working in the field of electrolyte membranes, fuel cell and laser physics.



reach the cathode for electrical current production.⁴ The prime component of the fuel cell is mainly the membrane electrode assembly (MEA), which consists of a gas diffusion layer, catalyst, and membrane.⁵ Focussing on the membrane situated between the anode and cathode, here membranes act as a conductor for the proton. The existing ions moved toward the cathode through the membrane by producing heat and water with free electrons. The mechanism of the fuel cell is depicted in Fig. 1.

Fuel cells are divided into five different types according to their operating system, *i.e.*, (i) Alkaline Fuel Cell (AFC) (ii) Phosphoric Acid Fuel Cell (PAFC) (iii) Molten Carbonate Fuel Cell (MAFC) (iv) Solid Oxide Fuel Cell (SOFC) and (v) Proton Exchange Membrane Fuel Cell (PEMFC).⁶ Various types of fuel cells and their properties are presented in Fig. 2. An ion-exchange membrane is used in various industrial process.⁷

Among membranes, PEMFC is a type of ion exchange membrane consisting of an ionic polymer carrying positive and negative charges in the moist state and enhancing the



Fig. 1 Schematic illustration of the fuel cell mechanism.

proton conductivity, corresponding reactions are provided in eqn (1)–(3),^{8–10}



First, Dupont developed the Nafion[®] membrane, which led to the large-scale manufacture with excellent conductivity and was used as a standard membrane for PEMFC.^{11–13} The structure of Nafion and its photographic image are shown in Fig. 3.

Nafion[®] exists in the form of a hydrophobic phase with the hydrophilic sulfonic acid.¹⁴ Water is the basic need as a charge carrier in an electrolyte membrane for PEMFC and DMFC. Such that the membranes should always be kept in a hydrated state for good performance, but it affects the power density and system efficiency, in case water gets low. However, perfluorinated polymers are still unsatisfactory due to (i) high cost of production (ii) difficulty to work at high temperatures (iii) high permeability for reactants.^{15–17} To overcome the drawbacks of Nafion, researchers have focused on the alternative polymers, which are suitable to



Karthikeyan Sekar

Karthikeyan Sekar is currently working as an Assistant Professor, at SRM Institute of Science and Technology, India. Previously he worked as Special Researcher at the University of Tokyo, Japan. He has received prestigious Japan Society for the Promotion of Science Invitational Fellowship 2022, and the Royal Society Newton International Alumni Grant 2021. Before that he has received the Japan Society for the Promotion of Science Postdoctoral Fellowship,

Japan (2018 to 2020), and the Royal Society Newton International Fellow (2016 to 2018), UK. His research interest is toward the development of carbon-based materials as catalysts for energy and environmental applications.



Dinakaran Kannaiyan

Dinakaran Kannaiyan is currently working as a Professor, in Department of Chemistry, Thiruvalluvar University, India. He has received prestigious JSPS Fellowship in 2006 and Brainpool invited scientist awarded by KRF, Government of South Korea in 2008. He is a member in Materials Research Society of India (IISC, Bengaluru) and Nano-Molecular Society of India (Hindustan College, Farah-Agra). His research interest includes polymer chemistry, nanohybrids and sensors.



Paradesi Deivanayagam

Paradesi Deivanayagam completed his PhD degree in Chemistry from University of Madras, Tamilnadu, India. He is currently working as an Assistant Professor in Department of Chemistry, SRM IST, Kattankulathur Campus, Tamil Nadu, India. His research interest towards development of polymer electrolyte membranes for fuel cell applications.





Fig. 2 Various types of fuel cells and their properties.



Fig. 3 Structure and image of Nafion membrane.

operate with HT-PEMFC and are also easy to synthesize in an economical way.^{18,19} Modifying Nafion with the additives such as CNT, silica, and functionalized clay blended with polymers have disadvantages in the form of cost and durability.²⁰ In order to prepare the alternative electrolyte to Nafion, the following are the essential characteristics to fulfill the requirements.²¹

- (i) Synthesize multiblock copolymer.
- (ii) High-proton conductivity.
- (iii) Cost-effective.
- (iv) Branched polymer.
- (v) Better oxidative stability.
- (vi) Capability to withstand MEA fabrication.

The non-fluorinated hydrocarbon polymers mainly the aromatic polymer with bulky groups route to a high-performance PEMFC.^{22,23} Many advantages are noticed for the hydrocarbon-based polymers when compared with PFSE polymers, including structure, eco-friendly synthesis, ease of modification, and of course being inexpensive.²⁴ Alternative membranes such as sulfonated polyether ketone (SPEEK), sulfonated polysulfone (SPSU), sulfonated polyphosphazene (SPPP), sulfonated polybenzimidazole (SPBI), sulfonated polyether sulfone (SPES), novel membranes are suitable for fabricating a working assembly in PEMFC.²⁵ Fig. 4 depicts the possible ways for the modification of polymer electrolyte membranes.

Among these polymers, several studies are focused on S-PEEK polymers with interesting features such as excellent mechanical strength, high thermal stability, low methanol permeability, adequate proton conductivity, ease to handle, and are economical. These properties had upgraded the SPEEK as a promising hydrocarbon-based polymers for PEM to operate in both PEMFC and direct methanol fuel cells (DMFC).^{26,27} Recently, SPEEK was used in batteries too. The research group of Chen *et al.* 2021 synthesized various modified SPEEK for the high-performance batteries.²⁸⁻³¹ It is a semi-crystalline polymer, amorphous in nature, and shows high thermal and chemical stabilities due to the presence of aromatic rings.³²⁻³⁴ It can be formed by post-sulfonation of commercial PEEK or pre-sulfonation by polymerization of various monomers in the synthesis method of (i) Friedel-craft acylation (ii) displacement reaction (iii) nickel-catalyzed coupling polymerization and (iv) ring-opening polymerisation involving monomers with sulfonic acid groups.³⁵



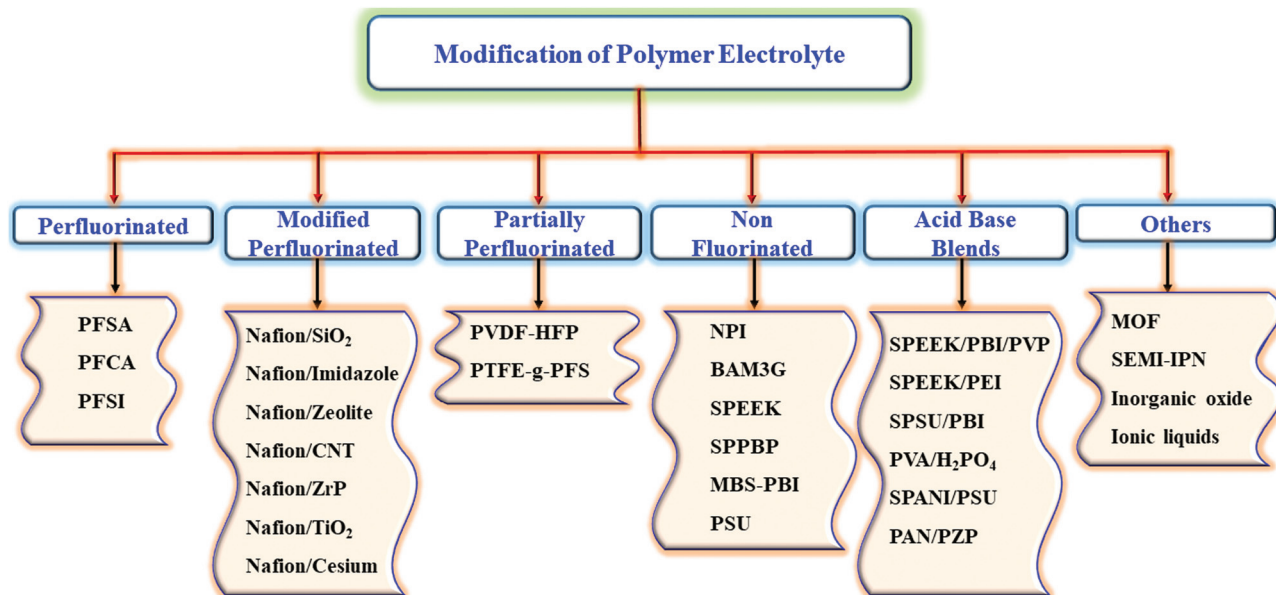


Fig. 4 Classifications of modified polymer electrolyte fuel cell membranes.

To enhance the stability of the SPEEK membrane, it has been blended with other polymers, inorganic fillers, inorganic metal oxide, clays, nanoparticles, *etc.*, The reason behind the incorporation of metal oxide into the polymers is to increase the membrane performance, such as selectivity, strength, permeability, hydrophilicity, conductivity, and ability to operate at HT-PEMFC.³⁶ This review article describes in detail the advantages and disadvantages of modified SPEEK membranes by fillers, additives, and blending with other polymers.

2. Post Sulfonation of PEEK

Sulfonation reaction is one of the most versatile techniques to modify aromatic polymers. The sulfonation of PEEK was obtained *via* direct sulfonation using concentrated sulphuric acid.³⁷ Initially, the PEEK powders were dried under vacuum for 12 h at 60 °C before sulfonation. The dried PEEK (2 g) was slowly added to 50 ml of concentrated sulphuric acid under continuous stirring at 30 to 40 °C for 1 h. After the addition of

PEEK, the reaction temperature was raised to 60 °C with vigorous stirring. Then, the solution was slowly cooled to room temperature followed by transferring to ice-cooled water through a dropping funnel. The yielded precipitate was washed several times with deionized water until the pH reached neutral and then dried at 105 °C for 24 h in a hot-air oven. The scheme for the preparation of SPEEK is displayed in Fig. 5.

The degree of sulfonation (DS) of SPEEK was maintained by varying the reaction time and temperature. It was proved that the water uptake ability and proton conductivity of SPEEK depended on the DS value.³⁸ It was shown that the increase in DS makes the polymer become more hydrophilic and absorbs more water, leading to the formation of water-mediated pathways for protons. In general, sulfonation of PEEK can be performed by the reagents concentrated sulphuric acid and chlorosulfonic acid. Even though the chlorosulfonic acid reagent was more advanced to an extent of sulfonation, it causes some degradation.³⁹ Hence, sulphuric acid is essentially used to carry out the sulfonation reaction as it is free from degradation.⁴⁰

2.1 Advantages over sulfonation

Poly(ether ether ketone) is a thermally stable, chemically resistant, and mechanically stable material. However, it cannot be directly used in fuel cell applications because of its fully hydrophobic segments. Hence, introducing the sulfonic acid group into PEEK polymer enhances the hydrophilicity, solubility in polar solvents, ion exchange capacity, and transport number. The solubility of the SPEEK membrane is reported as follows; (i) if the degree of sulfonation (DS) is around 30%, then it is soluble in DMF, DMAc, DMSO, and NMP under hot conditions only (ii) if the DS is around 40–70%, it is soluble in DMF, DMAc, DMSO, and NMP at room temperature (iii) if the DS is above 70%, it is soluble in methanol, and (iv) if the DS is 100%, it is soluble in hot water.⁴¹



Fig. 5 Schematic preparation of SPEEK membranes.



3. Modification of SPEEK

In general, the sulfonation of SPEEK polymer is very sensitive to the reaction conditions such as reaction time, temperature, and inert atmosphere. The degree of sulfonation decreases or increases if the conditions are not maintained properly. The higher DS of SPEEK material causes large swelling at high temperatures and finally, it dissolves in water. For this reason, cross-linked, hybrid, and composite membranes are being studied to improve their properties. Higher DS always favoured excellent ion exchange and proton conductivity. Two mechanisms are involved in the transportation of ions in electrolytic membranes *viz.*, (i) the Grotthuss mechanism and (ii) the vehicular mechanism. The clear proton transportation mechanism in the electrolyte membrane is presented in Fig. 6. Many studies have reported novel organic–inorganic composite membranes based on the SPEEK polymer.⁴²

3.1. SPEEK blend membranes

The blend membrane of SPEEK with different polymers will further alleviate the proton conductivity of the resultant electrolyte membranes, and meet the demands of stability and life cycle for the membranes during the fuel cell operation.

3.1.1 Blending with non-fluorinated membranes. Kanakasabai *et al.*⁴³ reported that the polyvinyl alcohol (PVA) cross-linked with sulfosuccinic acid (PVA–SSA) blended with the SPEEK (DS = 0.7) to prepare PVA–SSA/SPEEK composite membranes. The results revealed that the blended polymers showed high tensile strength, but the IEC and water uptake of the blend membrane were lower than the pristine membrane. It may be low DS and crosslinking of PVA in the occurrence of SPEEK, which may be hindering the PVA–SSA reaction. The presence of SPEEK and the crosslinking of the PVA with SSA in the blend seem to lead to higher thermal stability. Under the hydrated conditions, the proton conductivity of PVA–SSA/SPEEK (70/30) was found to be 0.070 S cm⁻¹.

Du *et al.*⁴⁴ have developed a sulfonated poly(phthalazinone ether sulfone ketone) (SPPEK) and SPEEK used to prepare the blend proton exchange membrane. The reported SPPEK/SPEEK membrane exhibits a low swelling ratio and good water uptake. The proton conductivity of the blend membrane was reported as 0.212 S cm⁻¹ at 80 °C.

3.1.2 Blending with Fluorinated membrane. Apart from non-fluorinated blend membranes, SPEEK with fluorinated blend membranes was prepared by Inan *et al.*⁴⁵ Water uptake and proton conductivity of the membranes were found to decrease with the addition of fluorinated polymers (PVDF–HFP). However, the reported proton conductivity of the SPEEK/PVDF–HFP membrane was sufficient to utilize the fuel cell operation. The characteristic results obtained from the blend membrane demonstrated that the non-fluorinated polymer blend with SPEEK showed excellent results for water uptake, swelling, and proton conductivity. Whereas, the fluorinated polymer blend with SPEEK is not much better but quite good.

Aygun *et al.*⁴⁶ in their study, prepared a high ionic conduction boron phosphate (BP) doped sulfonated poly(ether ether ketone)/poly(vinylidene fluoride) (SPEEK/PVDF) blend membrane. SPEEK/PVDF/10BP achieved the maximum power density (242 mW cm²) and current density (400 mA cm²) at 0.6 V. At 80 °C, the proton conductivity of the SPEEK/PVDF/10BP sample was measured to be 39 mS cm⁻¹. It was concluded that the addition of both the boron phosphate and the SPEEK/PVDF mix membrane showed promising outcomes for future fuel cell operations.

3.2 Cross-linked SPEEK by electron beam

Nowadays, the use of radiation for crosslinking in which an electron beam is widely used for polymers due to the advantage of insisting on the UV and thermal curing methods. The radiation cross-linking of the SPEEK membrane increased thermal, and mechanical properties, and maintained proton conductivity.



Fig. 6 Proton transport mechanism in the fuel cell.



Table 1 Comparison of IEC and proton conductivity of SPEEK-based PEM materials

Composite membranes	IEC (meq. g ⁻¹)	Proton conductivity (S cm ⁻¹)	Power density (mW cm ⁻²)	Ref.
SPEEK-SPI Blend-40	1.73	0.120 at 100 °C	—	67
SPEEK/EB/Y ₂ O ₃	—	0.080 at RT	—	68
SPEEK/BS/Y ₂ O ₃	—	0.010 at 90 °C	—	—
SPEEK-OMB (benzene silica)	—	0.079 at 80 °C	56	69
SPEEK-SSA (silica sulfuric acid)	1.19	0.130 at 80 °C	—	70
SPEEK-BP (copolymers)	—	0.000001 at 50 °C	—	71
SPKCL (cloisite 30B)	1.20*	0.0197 at 100 °C	—	72
SPEEK-SSA (silica sulphonic acid)	1.55	0.145 at 80 °C	—	73
SPEEK/Cloisite 15A/TAP	0.75	0.0004 at RT	213	74
SP/PPOSS (silsesquioxane)	—	0.043 at 80 °C	—	75
SPEEK/ZrP (zirconium phosphate)	—	0.079 at 150 °C	—	76
SPEEK/ZPMA (zirconium, phosphomolibdic acid)	—	0.072 at 80 °C*	—	77
SPEEK/sulfonated cyclodextrin	1.91	0.060 at 80 °C*	29.52	78
SPEEK/PVA/SGO/Fe ₃ O ₄	1.43	0.084 at RT	—	79
SPEEK-Cs-TPA (cesium-tungstophosphoric acid)	1.5*	0.130 at 50 °C	—	80
SPEEK-BPPO (Semi-IPN)	1.17	0.0029 at 50 °C	30	81
SPEEK-PAMPS-TiO ₂	2.03	0.090 at RT	283	82
SPEEK-PSSA-TiO ₂	1.98	0.075 at 25 °C	245	—
SPEEK-SZ (Sulfated Zirconia)	1.45	0.007 at 80 °C*	—	83
SPEEK/TPPS	2.01	0.038 at 30 °C	267	84
SPEEK/APDMS-grafted silica	1.57	0.120 at 80 °C*	—	85
SPEEK/Amine grafted silica	—	0.035 at RT	—	86
SPEEK-HPA MCM-41	—	0.007 at 140 °C	—	87
SPEEK/SiO ₂ -SiWA	—	0.048 at RT	—	88
SPEEK/Zeolite beta crystals	—	0.130 at 60 °C	10	89
SPEEK/AgGO-GO	—	0.037 at RT	—	90
SPEEK-PVB (nanofibre mat)	1.71	0.003 at 130 °C	—	91
SPEEK/PIL/PA	—	0.004 at 160 °C	—	92
SPEEK/PW ₁₁ V/rGO	—	0.064 at 65 °C	—	93
SPEEK/TiNFs	—	0.105 at 70 °C*	57.1	94
SPEEK/PES/Fe ₃ O ₄	0.33	0.0003	—	95
SPEEK/PES/TiO ₂	0.29	0.0004	—	—
SPEEK/PES/MoO ₃	0.31	0.0002 at RT	—	—
SPEEK/BaZrYO ₃	—	0.091 at 80 °C	44	96
SPEEK/SiWA/SO/AO	—	0.061 at RT	—	97
SPEEK-SiO ₂ -PANI	1.49	0.00036 at RT	—	98
SPEEK-ZrO ₂ -PANI	1.45	0.00033 at RT	—	—
SPEEK-TiO ₂ -PANI	1.51	0.00039 at RT	7.98	—
SPEEK-AIL	—	0.0069 at 120 °C	203	99
SPEEK/SGO	2.3	0.055 at 80 °C	378	100
SPEEK/ACNT	1.28	0.160 at 90 °C	96.02	101
SPEEK/FPAPB/Fe ₃ O ₄ -FGO	1.66	0.011 at 120 °C	—	102
SPEEK/SPVdF-HFP/GO	1.81	0.122 at 90 °C	—	103
SPEEK/CNC	1.74	0.186 at 95 °C	—	104
PEEK/sSrZrO ₃ @TiO ₂	1.16	0.121 at 80 °C	140	105
SPEEK/ZCO	1.46	0.009 at 30 °C	—	106
SPEEK/ZrO ₂ /PIL	—	0.660 at 750 °C	—	107

membrane swelling.¹⁰⁸ Xupo Liu *et al.* developed a diamine cross-linker on Semi-IPNs of BPPO/SPEEK Membranes for the direct methanol fuel cell. The SPEEK polymer chains were interpenetrated into semi-IPNs created by an alkylation reaction between bromo benzyl groups of bromomethylated poly(phenylene oxide) and amine groups of the 2,2'-(ethylenedioxy)bis(ethylamine) cross-linker.

The experimental results demonstrated that the semi-IPN has a significant impact on the membrane's dimensional stability, mechanical strength, and methanol-permeation resistance.¹⁰⁹ Paradesi *et al.*, prepared semi-IPN by polymerizing poly (ethylene glycol) diacrylate using benzoyl peroxide as an initiator with SPEEK. The impedance results showed the reduced proton conductivity with increasing content of PEGDA in Semi-IPN. However, the hydrolytic stability of semi-IPN membranes was higher than that of SPEEK, resulting in high performance and

hydrolytic stability of the PEG-based materials.¹¹⁰ Schematic illustration for the modification of the SPEEK matrix in various forms is presented in Fig. 7.

3.6 SPEEK-based MOF and ZIF

Current modification work on SPEEK has been focused on the metal-organic framework (MOF) and zeolite imidazole framework (ZIF). MOFs or metal-organic frameworks are a class of porous materials and their structures are usually made up of metal ions joined with organic ligands by coordination bonds. MOFs are being studied for a variety of applications, the most promising ones are mainly energy storage and gas separation.¹¹¹ Zhang *et al.*¹¹² used hybrid material of SPEEK/HPW@MIL101, which contains MOF MIL-101 (Cr), to prepare nanohybrid membranes for PEMFC applications. The ionic conductivity of the MOF-loaded composite membrane was 7.25 times higher





Fig. 7 Modification of SPEEK in various forms.

than that compared to the pristine SPEEK membrane. Leticia G. da Trindade *et al.*¹¹³ prepared SPEEK membrane with Zr-MOF by a casting method, and SPEEK/MOF composite membranes containing 7.5 wt% Zr-MOF exhibited high conductivity. The MOF's pore diameters aid in the aggregation of water molecules, which are held in place by hydrogen bonding within the pores.

ZIFs are a form of MOFs made up of tetrahedral metal ions (such as Zn^{2+} , Co^{2+} , Cu^{2+} , and others) and imidazole and ZIFs are regarded as a good addition in the application of polymer-based PEMs due to their superior chemical and thermal stability, high microporosity in the cavities, and unique imidazole ring structure.¹¹⁴ Fuqiang Hu *et al.*¹¹⁵ reported a new SPEEK-based proton exchange membrane made by incorporating as-prepared ZIF-COOH and the addition of ZIF-COOH, resulting in a significant improvement in the mechanical properties, proton conductivity, and methanol permeability. Fortunately, the SPEEK/ZIF-COOH-5 had a proton conductivity of 0.0152 S cm^{-1} at 80°C and tensile strength of 44.1 MPa, both were significantly higher than those of recast SPEEK. The generated SPEEK/ZIF composite membranes are shown to be potential candidates for promising PEM applications, and the prepared ZIF-COOH might be used to modify other polymers more efficiently.

4. Conclusion

Sulfonated poly (ether ether) ketone-based polymers are potential electrolyte membranes for fuel cell applications. This review article covered the recent work on the development of various SPEEK-based electrolyte membranes for use in PEMFC and DMFC applications. An ion exchange capacity and proton conductivity of SPEEK composite/blend membranes were compared to understand the suitability of these membranes for fuel cells. The major advantages of the SPEEK composite membrane include high proton exchange and low methanol crossover. Almost, all the SPEEK-related composite materials exhibited ionic conductivity in the order of $10^{-2} \text{ S cm}^{-1}$, which was sufficient to operate as a membrane in a hydrogen-oxygen fuel cell. In the future, an investigation is needed to focus on the rise of affinity toward membranes with water, as it increases the proton conductivity and to use appropriate inorganic particles. Also, this review highlighted the role of various metal oxides over the SPEEK matrix and it is concluded that the SPEEK-based membranes are one of the

remarkable proton-exchanging polymer electrolytes for use in fuel cells.

Conflicts of interest

There are no conflicts to declare.

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