Composite sPEEK with Nanoparticles for Fuel Cell's Applications: Review

Arief Rahman Hakim[a], Aprilina Purbasari[a], Tutuk Djoko Kusworo[a], Eniya Listiani Dewi[b]

[a] *Chemical Engineering Department, Diponegoro University*
Jl. Prof. Sudharto, S.H. Tembalang Semarang 50239. Telp +6224-7460058
[b] *Agency for the Assessment and Application of Technology, Center of Materials Technology BPPT*
Gd. II Lt. 22, Jl. M.H. Thamrin 8 Jakarta, 10340. Telp +6221-3169887
E-mail: *armir_05@yahoo.com (A.R.Hakim)*

Abstract:

The membranes in fuel cells must both conduct protons and serve as a barrier for fuel. This review discusses modifications nanoparticles of sPEEK (sulfonated polyether-ether ketone), sPEEK have advantages properties as fuel cell's membranes such as proton conductivity, mechanical strength, thermal stability, cheap, easily to handle and low fuel crossover. The main reason for researchers to modify with nanoparticles and adopt composite membrane of sPEEK in efforts to enhance properties of sPEEK, so composite allow a blending/modification to improve an overall material performance, several modification with effect by adding nanoparticles, such as with inorganic oxide, clay, zeolite, conductive polymers, protons conductive fillers.

Keywords: Fuel Cells, sPEEK, nanoparticles, composite, modification

1. Introduction

Fuel cells are converter of chemical energy to electricity with reduced pollution and environmental impacts **[1]**. Proton exchange membrane fuel cells (PEMFCs) and direct alcohol fuel cells (DAFCs) are possess several advantages over the other types of fuel cells like hydrogen-fed polymer electrolyte membrane fuel cells in the field of portable electronics and transportation usages **[18]**. Proton exchange membrane fuel cells (PEMFCs) operating at temperatures above 100^0C have in recent years been recognized as promising solutions to meet several technical challenges, such as CO poisoning, water management and cooling. To achieve high temperature operation of PEMFCs under ambient pressure, the ionic conductivity of the proton exchange membrane should not depend on high water content in the membrane.

The most investigated and applied fuel for PEMFCs is hydrogen **[6]**. This fuel can be obtained from a variety of feedstock e.g., fossil fuels, electrolysis of water with renewable or nuclear energy **[2]**. Hydrogen fuel cells produce only pure water as direct exhaust and the overall equation:

$$H_2 + 1/2\,O_2 \rightarrow H_2O \qquad \textbf{[1]}$$

These systems are highly efficient due to the relatively easy oxidation of hydrogen and this technology is developed to a large extent **[37]**. Also the flexible system design due to the connecting of fuel cell stacks is worth mentioning. These systems however remain expensive due to the noble metal catalyst and the high membrane costs. Other drawbacks can be found in, for instance, the hydrogen production. Ways of producing hydrogen results in high energy demands (electrolysis of water) or coherent emissions like CO2, NOx and SOx (e.g., natural gas-steam reforming, partial oxidation). Promising hydrogen sources to make PEMFC profitable are electrolysis of water by means of renewable energy sources or direct hydrogen production out of water with for example photo electrolysis. Other drawbacks are that hydrogen is a gas, and storage and distribution lead to severe problems due to high pressures or low temperatures needed for liquidization. Leakage can result in explosion danger when hydrogen is mixed with oxygen. In spite of these (to overcome) disadvantages, hydrogen is used in PEMFC technology mainly for stationary applications and transportation **[2, 37]**. It is widely accepted that hydrogen is not appropriate for the use in portable applications due to handling drawbacks of this fuel and low volume energy density.

Nowadays, methanol is chosen in the fuel cell community because it is a liquid with the advantages of easy storage and transportation. Methanol has a high carbon to oxygen ratio and an acceptable energy density. This type of PEMFCs is called the direct methanol fuel cell (DMFCs) and the overall reaction in this fuel cell type:

$CH_3OH + 3/2 O_2 \rightarrow 2H_2O + CO_2$ **[1]**

Portable application of fuel cells already penetrated the market and this market will grow extensively in the coming decade. Significant drawbacks of methanol are the low boiling point, the inflammability and toxicity. Leakage during application could lead to severe health problems **[20]**.

Therefore, the use of ethanol as a fuel for portable applications is becoming more and more of interest **[20]**. This PEMFC is called the direct ethanol fuel cell (DEFCs). Ethanol is a generally accepted substance, non-toxic, and the infrastructure for ethanol distribution already exists to a large extent. It has a higher energy density than methanol as well as a higher boiling point, and the overall reaction in this fuel cell type:

$C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2$ **[1, 20]**

Many other fuels have been proposed in literature for application in direct liquid fuel cells. Most of them are hydrocarbons bearing oxygen-groups in the form of alcohols, ethers, and acids.

They have proton exchange membrane (PEM) as a key component in the system and has function as an electrolyte for transferring protons from anode to the cathode, also as a barrier to the passage of electrons and fuel cross-leaks between the electrodes. The review focus has been on developing PEM, considerable efforts to develop alternative PEM materials have been proposed.

A suitable polymer electrolyte membrane (PEM) should fulfill the following requirements **[15]**:

a. High proton conductivity.
b. Good electrical insulation.
c. High mechanical and thermal stability.
d. Good oxidative and hydrolytic stability.
e. Cost effectiveness.
f. Good barrier property.
g. Low swelling stresses, and
h. Capability for fabrication in membrane electrode assembly (MEA)

2. Choice of Polymer Electrolyte Membranes for Fuel Cells

In order to qualify as membrane materials for electrolysis and fuel cell applications, polymer electrolyte membranes must possess excellent chemical and environmental resistance, especially against attack of oxygen or strong acids, high thermal and dimensional stabilities and high ion conductivity. Introducing sulfuric acid group in the polymeric membranes often brings about this ion conductivity. Per fluorinated polymer electrolytes (Nafion) exhibit a prolonged service life under extreme reaction conditions. However, most of the per fluorinated membranes being expensive and difficult to process, there is a demand for novel thermally and chemically stable polymer electrolytes combining membrane properties of per fluorinated polyelectrolyte (Nolte et al. 1993). Disadvantages of per fluorinated ionomers (PFI) membranes stimulated efforts to synthesize polymer electrolyte membrane (PEM) based on partially fluorinated and fluorine free hydrocarbon ionomers membranes such as aromatic polyether ether ketone (PEEK) **[40]**.

2.1 Sulfonation of PEEK (sPEEK)

Sulfonation is a versatile route to polymer modification that is essentially suitable for aromatic polymers. Main purpose of sulfonating an aromatic PEEK is to enhance acidity and hydrophilicity as the presence of water facilitates proton transfer and increases conductivity of solid electrolytes. At 100% sulfonation, sPEEK can dissolve in water, implying its higher hydrophilicity. Among the attractive properties of engineering thermoplastic sPEEK, good solvent resistance, high thermo-oxidative **[17]** stability and good mechanical properties are significant. Sulfonation is an effective method to increase both the permeation rate of water vapor and the separation factor of water vapor over gases sPEEK can be sulfonated with a sulfonation degree of 1.0 per repeat unit. However, a greater degree of sulfonation (DS) is difficult to achieve due to insolubility and side reactions such as inter polymer cross-linking and degradation. Sulfonation of PEEK can be performed by concentrated sulfuric acid, chlorosulfonic acid, by pure or complexes sulfur trioxide, by acetyl sulfate and methane sulfuric acid. Sulfonated polymers can be prepared as free acid form (SO_3H^-), salts ($SO_3^-Na^+$), esters (SO_2R^-) and various derivatives. Sulfonation increasingly hindered with decreasing ether group content of polymer chain (PEEK<PEEKK/PEK<PEKEKK).

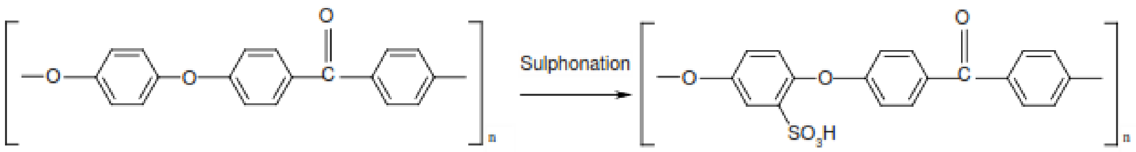

Figure 1.Reaction sulfonation poly ether-ether ketone (sPEEK) **[3]**

2.2 Advantages of Introducing SO_3H- Group

By introducing SO_3H^- groups in PEMs, ion exchange capacity, hydrophilicity, solubility in polar solvents, proton conductivity and transport number of PEMs increases. Important parameter for sulfonated PEEK is its ion exchange capacity and swelling capacity.

2.3 Composite Sulfonated Polyether-ether ketone (sPEEK)

Sulfonated aromatic poly (ether ether ketone) has been explored as possible substitutes for Nafion due to their low cost, excellent mechanical and thermal properties, and high conductivities. Further, they can be easily functionalized for application as fuel cell membranes. Among aromatic polymers, hydrophobic poly (ether ether ketone) (PEEK) is the most studied because of higher thermal and chemical stability and it also offers appreciable proton conductivity when sufficiently sulfonated. However, the shortcoming of these membranes is that their, both mechanical and chemical properties deteriorate with increasing sulfonation. Highly sulfonated materials show large swelling at high temperatures finally leading to membrane dissolution in water. Therefore, cross-linked, hybrid or composite polymers are being studied to improve these properties. Recently, a series of organic–inorganic composite membranes based on sPEEK were reported. Classifications of polymer electrolyte membrane are fluorinated membrane, hydrocarbon membrane, aromatic membrane, hybrid/composite membrane.

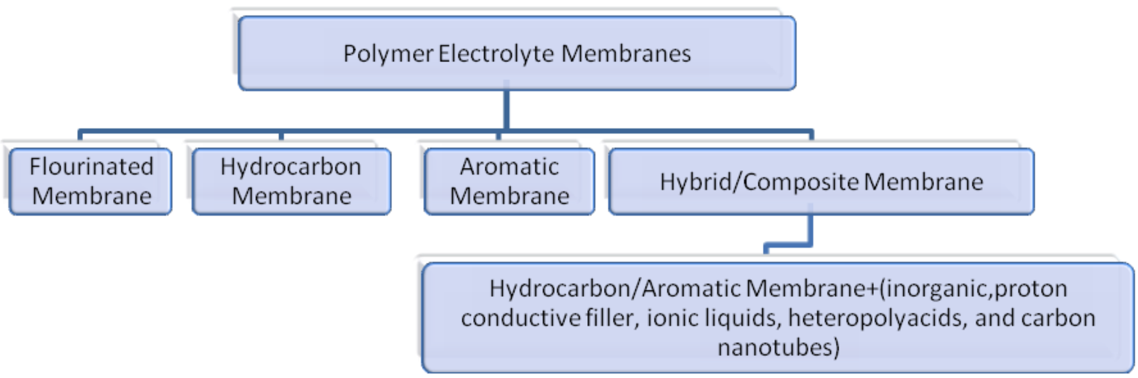

Figure 2.Classification of polymer electrolyte membranes based on materials **[32]**.

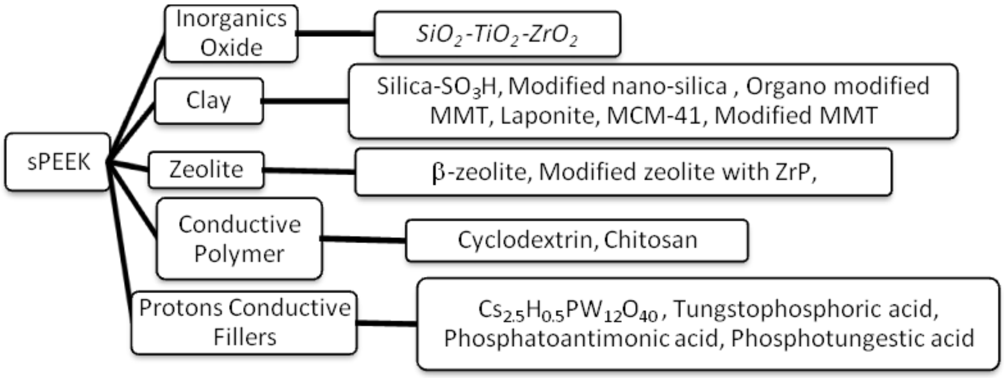

Figure 3.Modification sPEEK as hybrid/composite membrane for fuel cells applications **[30]**.

The new alternative membrane should have excellent chemical resistance, high thermo oxidative stability, good mechanical properties, can be operated at high temperature, high proton conductivity at lower water contents, and reduce fuel crossover (especially methanol). New membrane technology can be subdivided into the following three areas, post-reactions on polymers to form ion conducting membranes, direct copolymerization of ion containing monomers to form ion conducting polymers, and composite structures based on polymer/polymer composites or polymer/inorganic composites. Each area has certain advantages and the new membranes have much more specific operating targets than a “one size fits all” approach.

Addition of nanoparticles into the sPEEK matrix is also an important approach in PEM research. This approach has two objectives: one is to improve the mechanical properties of the composite membranes and the other is to physically counteract fuel crossover. It has also been suggested that the size of the particles (nano or micro), surface properties (acid or basic), and the fictionalization determine whether the filler, besides acting as a reinforcing components as above mentioned, can impart a significant improvement in proton conductivity.

Nanocomposites are a new class of composites that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. One can distinguish three types of nanocomposites, depending on how many dimensions of the dispersed particles are in the nanometer range. When the three dimensions are in the order of nanometers, we are dealing with isodimensional nanoparticles, such as spherical silica nanoparticles obtained by in situ sol-gel methods or by polymerization promoted directly from their surface, but also can include semiconductor nanoclusters. When two dimensions are in the nanometer scale and the third is larger, forming an elongated structure, we speak about nanotubes or whiskers as, for example, carbon nanotubes or cellulose whiskers, which are extensively studied as reinforcing nanofillers yielding materials with exceptional properties.

In this review, there were so many materials or filler had been tried to develop a new composites membrane sPEEK and effects on membrane performance during the modification of sPEEK membranes are summarized.

Table 1. Influence on membrane performances during the sPEEK modification

Combination	Conclusions	References	Application
sPEEK/BPO_4	Reasonable conductivity compared to Nafion composites at 100-140 °C.	**[24]**	DMFCs
sPEEK/α-ZrP	No appreciable improvement over sPEEK.	**[26]** **[31]**	DMFCs
sPEEK/ZrO_2	More than one order of magnitude reduction in methanol permeability and conductivity.	**[26]** **[31]**	PEMPCs, DMFCs
sPEEK/silica	Reduction in H_2O permeability without a significant decrease in conductivity.	**[26]**	DMFCs

sPEEK/α-ZrP /ZrO_2	Large reduction in methanol permeability without a large conductivity sacrifice.	**[26]**	DMFCs
sPEEK/ SiO_2/TiO_2/ZrO_2	Methanol and water permeability are reduced with the addition of inorganic materials.	**[26]**	PEMPCs, DMFCs
sPEEK / Zirconium Phosphate (ZrP)	Swelling studies were performed in water, sulfuric acid and methanol/water. The methanol permeability and proton conductivity were increased.	**[31]**	DMFCs
sPEEK/ Laponite/ MCM 41	The modification of nanofillers induced better compatibility with polymer thus reducing methanol permeability. It also increased the proton conductivity.	**[16]**	DMFCs
sPEEK / Boron Phosphate (BPO_4)	Improvement of methanol crossover.	**[19]**	DMFCs
sPEEK/ PWA	Proton conductivity was higher than the pure sPEEK membrane even though the water uptake was lower.	**[36]**	DMFCs
sPEEK / Chitosan	Cross linked CS layer onto the sPEEK surface was an effective method for improving the performance of the sPEEK membrane, especially for reducing the methanol crossover.	**[42]**	DMFCs
sPEEK/ sMMT	The membrane stability in water and methanol aqueous solution, as well as the mechanical stability increases with the sMMT loading content whereas thermal stability does not improve significantly. The methanol permeability reduction is obtained when the sMMT loading content increases for various methanol concentrations.	**[10]**	DMFCs
sPEEK/ TiO_2	Composites with hydrophilic titanium particles present an <u>inhomogeneous</u> microstructure with agglomeration of TiO_2 particles, high strength and low ductility, high water uptake and proton conductivity. Composites with hydrophobic titanium particles have a very <u>homogeneous</u> microstructure, very reproducible mechanical properties, and lower water uptake and proton conductivity.	**[3]**	PEMFCs
sPEEK/ ZPMA	Proton conductivity of composite membranes was much higher than that of pure sPEEK membrane due to high conducting property of phosphomolibdic acid, methanol permeability was still very low and comparable to that of pristine. Composite membrane had much lower water uptake than the pure sPEEK membrane, it was dimensionally stable in hot water even above 80 ^{0}C.	**[22]**	DMFCs
sPEEK/ Reactive Organoclay	The membrane stability liquid uptake in water and methanol, oxidative stability as well as mechanical and thermal stability significantly improve with incorporation of reactive organoclay into the cross-linked sPEEK polymer matrix, without affecting the proton conductivity appreciably.	**[11]**	PEMFCs, DMFCs
sPEEK/ Hydrate Tin *($SnO_2.nH_2O$)*	The polymer electrolyte membrane with 50 wt% SnO2·*n* (H_2O) possess good proton transport characteristics, reduced methanol uptake and improved stability compared to unfilled membrane.	**[23]**	DMFCs
sPEEK/ CeO_2	The proton conductivity better than that without treatment. The methanol permeation coefficient of membrane specimens decreased with increasing CeO_2 contents and furthermore reduced by about 20% after treated with perpendicular high magnetic field. The water uptake of membrane specimens decreased with CeO_2 doping, but would not be influenced by the magnetic field.	**[35]**	DMFCs
sPEEK/ SiO_x-S	Composite membranes have good dimensional stability, high proton conductivity, and low methanol permeability.	**[8]**	DMFCs

sPEEK/ Y_2O_3	Proton conductivity was higher than pure sPEEK, water uptake, thermal stability and tensile stress increased.	**[43]**	DMFCs, PEMFCs
sPEEK/ β-Zeolite	Conductivity of the composite membrane containing of zeolite beta filled sPEEK increase. Among the zeolite beta /sPEEK composite membranes the best conductivity results were achieved with zeolite beta having a SiO_2/Al_2O_3 ratio of 50 at 10 wt.% loading.	**[7]**	DMFCs
sPEEK/ Lacunary divacant $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$	Organic-inorganic composites more stable than plain membrane, low methanol crossover, but low proton conductivity.	**[27]**	DMFCs
sPEEK/OMMT	The methanol permeability of the composite membranes decreases significantly, higher proton conductivity at 90^{0}C than Nafion®115. Offer a low-cost alternative to the per fluorinated membranes.	**[9]**	DMFCs
sPEEK/SiO_2/ZrP	The sPEEK/SiO_2/ZrP (80/10/10 %) composite membranes showed a methanol permeability, lower than that of the sPEEK and Nafion117 membrane, and highest OCV	**[41]**	DMFCs
sPEEK/MMT Clay	Composites membrane with 62% of sulfonation and 1.0 wt. % MMT loading showed membrane selectivity of approximately 8500 compare to 4500 of Nafion 117	**[12]**	PEMFCs, DMFCs
sPEEK/Silica with sol-gel polyethoxysiloxane (PEOS)	Proton conductivity of the composite membranes is higher than the pure. The samples prepared with low PEOS content (10 and 20 wt. %) are more stable upon successive heating/cooling measuring cycles, showing less dependency on membrane hydration than the pure sPEEK.	**[1]**	PEMFCs, DMFCs
sPEEK/Tungstosilicic acids (SIWA) loaded SiO_2-Al_2O_3	High water uptake and proton conductivity (maximum value 6.1×10^{-2} Scm^{-1}). Low methanol permeability values were recorded for the membranes.	**[13]**	DMFCs
sPEEK/ Cs-Tungstophosphoric acid (Cs-TPA)	The methanol permeability was decreased for sPEEK (DS: 60%) with 10% wt. Cs-TPA membrane, and increase proton conductivity was achieved at 80 ^{0}C under 100% RH. The weight loss at 90 ^{0}C increased with the addition of inorganic particles, as expected. The hydrolytic stability of the sPEEK/Cs-TPA based composite membranes was improved with the incorporation of the Cs-TPA particles into the matrix. Composite membranes were hydrolytically more stable than sPEEK70/Cs-TPA composite membranes. On the other hand, methanol, water vapor, and hydrogen permeability values of sPEEK60 composite membranes were found to be lower than that of Nafion.	**[4]**	PEMFCs, DMFCs
sPEEK/ Montmorilonite-Silicotungstic Acid (MMT-STA)	Water uptake and proton conductivity at ambient temperature and 100% relative humidity of the composite membranes were higher than the pristine sPEEK membrane 50 % wt. STA-MMT respectively. Methanol permeability of the developed membranes in this study was lower than the Nafion 112 membrane.	**[14]**	DMFCs
sPEEK/Silica Sulfuric Acid (SSA)	The water uptakes of the composite membranes in water and under low relative humidity's are all higher than that of the pristine sPEEK membrane. The composite membrane containing 5 wt. % SSA exhibits the highest conductivity. Approximately 18.6 % higher than that of the pristine sPEEK membrane and 8.6 % higher than that of Nafion117. The composite membranes also show good thermal stability.	**[5]**	PEMFCs

sPEEK/ $AlPO_4$	Composite membranes showed better thermal stability compared to pure sPEEK membranes. Water uptake and proton conductivity of the composite sPEEK membranes were found to be lower than that of pure sPEEK membranes, while the composite membranes exhibited a better swelling behavior and mechanical stability than the pure sPEEK samples.	**[28]**	PEMFCs
sPEEK/ Ferrierite Zeolite (CP914, Zeolite with a molar ratio SiO_2/Al_2O_3 of 20)	Methanol permeability, thermal, mechanical properties, and proton conductivity of composite membranes were measured for the effect of Ferrierite zeolite as inorganic filler at various amounts (5, 10, 15, 17, and 20% v/v). The proton conductivity and methanol permeability values of the composite membranes were measured compared to those of a commercial membrane, Nafion 117.	**[34]**	DMFCs
sPEEK/ Dihydrogenimidazole modified silica (DHIM)	The proton conductivity as well as the proton diffusion coefficient as a function of modifier content showed a linear decrease. High selectivity of proton diffusion coefficient to ethanol permeability coefficient was obtained with high modifier concentrations. At low modifier concentrations, this selectivity was dominated by ethanol permeation and at high modifier concentrations by proton diffusion.	**[29]**	DAFCs, DEFCs
sPEEK/Sulfonated Cyclodextrin	High proton conductivity and low methanol permeability brought a very high selectivity. Moreover, methanol permeability of these membranes decreased with the increase of the methanol concentration. Thus, the membranes are attractive to be used at high methanol concentration and the higher power density and higher specific energy is hopeful to come true.	**[39]**	DMFCs

3. Treatment composite sPEEK

The fabrication of composite polymer electrolyte membrane sPEEK with adding inorganic oxide, clay, zeolite, conductive polymer and protons conductive fillers are considered to be the most promising development in polymer electrolyte membrane (PEM) for PEMFCs or DAFCs application could enhance the properties of polymer membrane. When the composite has the potential to be balance between two important characteristics at polymer electrolyte membrane performance, proton conductivity and fuel crossover becomes it's even more attractive. Therefore special attention has to given to composite techniques in developing electrolyte membrane since these techniques have proven their effectiveness. For instant, the function of acidity of inorganic filler is able to facilitate the proton transfer mechanism of the membrane, clay/montmorilonite can reduce fuel crossover and stable to high temperature.

Mikhailenko et al. was fabricated sPEEK-BPO_4 with various degree of sulfonation (50%, 72%, 80%) and adding BPO_4 (0%, 20%, 40%, 60%) with membrane casting methode, BPO_4 is inexpensive solid made by simple reaction between phosphoric and boric acid, the result optimum was water uptake 105 wt. % dan conductivity at 100^0C 49.10^3 S/cm with combination degree of sulfonation 72% with 60% BPO_4.

Nunes et al. prepared composite membrane with inorganic modification of sPEK, sPEEK by in situ hydrolysis of different alkoxides of Si, Ti, and Zr. SiO_2 improved by CDI (1,1'-Carbonil-diimidazole) and AS (1-3-aminopropyl-silane). Then introduced precursor $Zr(OPr)_4$ sPEEK (DS 85%), water and methanol crossover was reduced without diminishing the conductivity to the same extend.

Composites of sPEEK with surface-functionalized hydrophilic (Tri-hydroxymethyl-propane)-TiO_2 show large agglomeration of oxide particles and an inhomogeneous microstructure, the agglomeration titanium particles with segregation of sulfonic acid groups give high proton conductivity, and hydrophobic (silicone oil)-TiO_2 present a very homogeneous microstructure with well dispersed oxide nanoparticles. This composite membranes result low proton conductivity **[3]**.

Adding Y_2O_3 **[43]** or CeO_2 **[13]** and $SnO_2.nH_2O$ **[23]** were the same method can resulting water uptake property was slightly improved, higher tensile strength but lower elongation at break, the thermal stability of membrane higher than that of the pure sPEEK.

Modification cross-linked sPEEK/reactive organoclay nanocomposite membranes with solution intercalation method, which cloisite-30B modified with N-methyl tallow bis-hydroxyethyl quaternary ammonium used as organoclay **[11]**, result for this modification was showed higher tensile strength, modulus and lower elongation at break compared to pristine and neat cross-linked sPEEK. Water and methanol uptake higher than pristine sPEEK and cross linked sPEEK. Other hand, with the same method, modification clay (montmorilonite (MMT)), membrane based on sPEEK and 1 wt. % of MMT **[12]**, as the optimum nanoclay composition, exhibits a high selectivity and power density at the concentrated methanol feed, higher open circuit voltage (OCV), and convenient process ability and low cost.

Other alternative also low cost for membrane fuel cells, fabrication sPEEK with β-zeolite with composition optimum aluminosilicate SiO_2/Al_2O_3 ratio of 50 at 10 wt.% **[7]**. This membrane also have thermal, chemical, mechanical strength stability, various blending with Poly ether sulfone (PES) can improved thermo hydrolytic stability.

Current modification work on sPEEK has been devoted to the additives of silica, zeolite, and clay. Up to now, no research has been reported about the addition of β-cyclodextrin **[39]** in sPEEK membranes. The β-cyclodextrin is a water soluble cyclic oligosaccharide that consists of seven glucose units linked by 1,4-glucosidic bonds. From the molecule structure point of view, cyclodextrin is natively selective to water than methanol. The multi-hydroxy of β-cyclodextrin can be easily modified by other groups such as sulfuric anion. Thus, the sulfonated cyclodextrin may be the potential proton conducting material with low methanol permeability. However, the cyclodextrin and sulfonated cyclodextrin cannot be fabricated into a practical membrane due to their solubility in water. To bring their advantages into play, we blended the sulfonated cyclodextrin into Nafion® membranes. Their investigation demonstrated that the addition of cyclodextrin can reduce methanol crossover effectively. In our previous study, sulfonated cyclodextrin has been successfully introduced into polyvinyl alcohol membrane to serve as a proton conductor and its beneficial effects have been investigated and discussed, and then result for this method, the modification work on the existing membrane material such as sPEEK is looking for the suitable additives. The compatibility, accessibility and easy to realize mass production should also be considered. We report here the blend membranes based on sPEEK and sulfonated cyclodextrin, also displayed was their preliminary performance in DMFC application. The blend membranes can be fabricated by a solution casting method easily.

Recent research about sPEEK was blended with sPES (Sulfonated Poly ether sulfone) used membrane in VRB (Vanadium redox battery) **[38]**, the results indicate that sPES/sPEEK membrane possesses significantly strong mechanical strength, high water uptake and low permeability of VO^{2+} ions. The performance of VRB single cell with sPES/sPEEK membrane shows significantly lower charge capacity loss, higher coulombic efficiency (CE) and energy efficiency (EE) (98% vs. 91% and 84% vs. 79.5%, respectively) compared to that with Nafion 212 membrane. Furthermore, the sPES/sPEEK membrane presents good cell performance up to 100 cycles (more than 265 h) with no significant decline in CE and EE.

Conclusion

Comparative study of modification nanoparticles to make sPEEK composites with adding inorganic oxide, clay, zeolite, conductive polymers, and proton conductive fillers can enhance properties of sPEEK such as fuel crossover, proton conductivity, and mechanical strength. Their modification was compatible to use as membranes for PEMFCs, DMFCs, DEFCs, also VRB.

References

Journals :

[1]. Colicchio I, Demco DA, Baias M, Keul H, Moeller H. 2009. Influence of the silica content in sPEEK–silica membranes prepared from the sol-gel process of polyethoxysiloxane: Morphology and proton mobility, *Journal of Membrane Science*, 337 : 125-135.

[2]. Conte M, Lacobazzi A, Ronchetti M. 2001. Hydrogen economy for a sustainable development: state-of-the-art and technological perspectives, *Journal Power Sources*, 100 (1-2): 171.

[3]. DiVona ML, Sgreccia E, Donnadio A, Casciola M, Chailan JF, Auer G, Knauth P. 2011. Composite polymer electrolytes of sulfonated polyether ether ketone (sPEEK) with organically functionalized TiO_2. *Journal of Membrane Science*, 369: 536-544.

[4]. Dogan H, Inan TY, Unveren E, Metin KM. 2010. Effect of cesium salt of tungstophosphoric acid (Cs-TPA) on the properties of sulfonated polyether ether ketone (sPEEK) composite membranes for fuel cells applications. *International Journal of Hydrogen Energy*, 35: 7784-7795.

[5]. Du L, Yan X, He G, Wu X, Hu Z, Wang Y. 2012. Sulfonated poly (ether-ether ketone)sPEEK proton exchange membranes modified with silica sulfuric acid nanoparticles. *International Journal of Hydrogen energy,* xxx: 1-9.

[6]. Edwards PP, Kuznetsov VL, David WIF. 2008. Hydrogen and fuel cells: towards a sustainable energy future, *Energy Policy*, 36 (12): 4356.

[7]. Eroglu I, Sengul E, Erdener H, Akay RG, Yucel H, Bac N. 2009. Effects of sulfonated polyether-ether ketone (sPEEK) and composite membranes on the proton exchange membrane fuel cell (PEMFC) performance, *International Journal of Hydrogen Energy,* 34: 4645-4652.

[8]. Gao Q, Wang Y, Xu L, Wei G, Wang Z. 2009. Proton-Exchange Sulfonated poly (ether ether ketone) (sPEEK)/SiOx-S composite membranes in direct methanol fuel cells (DMFC). *Separation Science And Engineering Chinese Journal of Chemical Engineering*, 17(2):207-213.

[9]. Gaowen Z, Zhentao Z. 2005. Organic/inorganic composite membranes for application in direct methanol fuel cells (DMFC). *Journal of Membrane Science*, 261:107–113.

[10]. Gosalawit R, Chirachanchaia S, Shishatskiy S, Nunes SP. 2008. Sulfonated montmorillonite/ sulfonated poly (ether-ether ketone) (sMMT/sPEEK) nanocomposite membrane for direct methanol fuel cells (DMFCs). *Journal of Membrane Science,* 323: 337-346.

[11]. Hande VR, Rath SK, Rao S, Patri M. 2011. Cross-linked sulfonated poly (ether ether ketone) (sPEEK)/reactive organoclay nanocomposite proton exchange membranes (PEM). *Journal of Membrane Science*, 372: 40-48.

[12]. Hasani-Sadrabadi MM, Emami SH, Ghaffarian R, Moaddel H. 2008. Nanocomposite Membranes Made from Sulfonated Poly (ether-ether ketone) and Montmorillonite Clay for Fuel Cells Applications. *Energy & Fuels* 22: 2539-2542.

[13]. Ismail AF, Othman NH, Mustafa A. 2009. Sulfonated poly (ether-ether ketone) (sPEEK) composite membrane using tungstosilicic acid supported on silica–aluminum oxide for direct methanol fuel cell (DMFC). *Journal of Membrane Science,* 329: 18-29.

[14]. Ismail AF, Mohtar SS, Matsuura T. 2011. Preparation and characterization of sPEEK/MMT-STA composite membrane for DMFC application, *Journal of Membrane Science*, 371: 10-19.

[15]. Jones DJ, Rozière J. 2008. Advances in the development of inorganic–organic membranes for fuel cells applications. *Advanced Polymer Science*, 215: 219-64.

[16]. Karthikeyan CS, Nunes SP, Prado LASA, Ponce ML, Silva H, Ruffmann B, Schulte K. 2005. Polymer nanocomposite membranes for DMFC application. *Journal of Membrane Science*, 254: 139-146.

[17]. Kopitzke RW, Linkous CA, Nelson GL. 2000. Thermal stability of high temperature polymers and their sulfonated derivatives under inert and saturated vapor conditions, *Polymer Degradation Stability*, 67: 335-344.

[18]. Kreuer KD. 2000. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *Journal of Membranes Science*, 185: 29-39.

[19]. Krishnan P, Park JS, Kim CS. 2006. Preparation of proton conducting sulfonated poly(ether ether ketone)/boron phosphate (BPO_4) composite membranes by an in-situ sol-gel process. *Journal of Membrane Science*, 279: 220.

[20]. Lamy C, Lima A, LeRhun V. 2002. Recent advances in the development of direct alcohol fuel cells (DAFC). *Journal Power Sources*, 105 (2): 283.

[21]. Li W, Zhang F, Yi S, Huang C, Zhang H, Pan M. 2012. Effects of casting solvent on microstructure and ionic conductivity of anhydrous sulfonated poly (ether ether ketone)-inoic liquid composite membranes, *International Journal of Hydrogen Energy* 37: 748-754.

[22]. Luu DX, Kim D. 2011. sPEEK/ZPMA Composite Proton Exchange Membrane for Fuel Cells Application, *Journal of Membrane Science*, 371: 248-253.

[23]. Mecheri B, D'Epifanio A, Traversa E, Licoccia S. 2008. Sulfonated polyether ether ketone and hydrated tin oxide proton conducting composites for direct methanol fuel cell applications. *Journal of Power Sources*, 178: 554–560.

[24]. Mikhailenko SD, Zaidi SMJ, Kaliaguine S. 2001. Sulfonated poly (ether-ether ketone based composite polymer electrolyte membranes. *Catalysis Today*, 67: 225-236.

[25]. Nolte R, Ledjeff K, Bauer M, Mülhaupt R. 1993. Partially sulfonated poly (arylene ether sulfone) - A versatile proton conducting membrane material for modern energy conversion technologies, *Journal Membranes Science*, 83: 211-220.

[26]. Nunes SP, Ruffmann B, Rikowski E, Vetter S, Richau K. 2002. Inorganic modification of proton conductive polymer membranes for direct methanol fuel cells, *Journal of Membrane Science*, 203: 215–225.

[27]. Ponce ML, Prado LASA, Silva V, Nunes SP. 2004. Membranes for direct methanol fuel cells based on modified heteropolyacids, *Desalination*, 162: 383-391.

[28]. Rangasamy VS, Thayumanasundaram S, Greef ND, Seo JW, Locquet JP. 2012. Preparation and characterization of composite membranes based on sPEEK And $AlPO_4$ for PEMFCs. *Solid State Ionics,* 216: 83-89.

[29]. Roelofs KS, Hirth T, Schiestel T. 2011. Dihydrogenimidazole modified silica-sulfonated poly(ether ether ketone) hybrid materials as electrolyte membranes for direct ethanol fuel cells, *Materials Science and Engineering B* 176: 727-735.

[30]. Rowshanzamir S, Peighambardoust SJ, Amjadi M. 2010. Review of the proton exchange membranes for fuel cell applications, *International Journal of Hydrogen Energy*, 35: 9349-9384.

[31]. Ruffmann B, Silva H, Schulte B, Nunes SP. 2003. Organic/inorganic composite membranes for Application in DMFC. *Solid State Ionics*, 269: 162-163.

[32]. Shahi VK, Tripathi BV. 2011. Organic–inorganic nanocomposite polymer electrolyte membranes for fuel cell applications, *Progress In Polymer Science*, 36: 945-979.

[33]. Silva VS, Schirmer J, Reissner R, Ruffmann B, Silva H, Mendes A, Madeira LM, Nunes SP. 2005. Proton electrolyte membrane properties and direct methanol fuel cell performance II. Fuel cell performance and membrane properties effects, *Journal of Power Sources*, 140: 41–49.

[34]. Sirivat A, Auimviriyavat J, Changkhamchom S. 2011. Development of Poly(ether ether ketone) (PEEK) with inorganic filler for direct methanol fuel cells (DMFCs). *Industrial Engineering Chemistry Research*, ACS Publications. dx.doi.org/10.1021/ie2006005.

[35]. Tong JY, Guo Q, Wang XX. 2009. Properties and structure of sPEEK proton exchange membrane doped with nanometer CeO_2 and treated with high magnetic field. *eXPRESS Polymer Letters* Vol.3, No.12: 821-831.

[36]. Wang Z, Ni H, Zhao C, Li X, Fue T, Na H. 2006. Investigation of Sulfonated Poly (ether ether ketone sulfone)/ Heteropolyacid Composite Membranes for High Temperature Fuel Cell Applications. *Polymer Science: Part B: Polymer Physics*, 44: 1967-1978.

[37]. Wee JH. 2007. Applications of proton exchange membrane fuel cell systems, *Renewable Sustainable*, Energy Rev., 11 (8): 1720.

[38]. Yan C, Ling X, Jia C, Liu J. 2012. Preparation and characterization of sulfonated poly (ether sulfone)/sulfonated poly(ether ether ketone) blend membrane for vanadium redox flow battery, *Journal of Membrane Science*, xx: xxx.

ISBN : 978-602-097-281-7

[39]. Yang T, Liu C. 2011. sPEEK/sulfonated cyclodextrin blend membranes for direct methanol fuel cell, *International Journal of Hydrogen Energy*, 36: 5666-5674.

[40]. Zaidi SMJ, Mikhailenko SD, Robertson GP, Guiver MD, Kaliaguine S. 2000. Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications. *Journal Membranes Science*, 173: 17-34.

[41]. Zhang H, Fan X, Zhang J, Zhou Z. 2008. Modification research of sPEEK membranes used in DMFCs. *Solid State Ionics*, 179: 1409-1412.

[42]. Zhong S, Cui X, Fu T, Na H. 2008. Modification of sulfonated poly (ether ether ketone) proton exchange membrane for reducing methanol crossover, *Journal of Power Sources*, 180: 23-28.

[43]. Guo Q, Chen j, Li D, Tong J, Li X. 2012. Properties of sPEEK based proton exchange membranes by doping of ionic liquids and Y_2O_3. *Progress in Natural Science: Materials International*, 22(1): 26-30

Books :

[1] Sekhawat D, Spivey JJ, Berry DA. 2011. Fuel Cells : *Technologies for Fuel Processing*. Elsevier, Amsterdam