



Cross-linked sulfonated poly(ether ether ketone)-poly ethylene glycol/silica organic–inorganic nanocomposite membrane for fuel cell application

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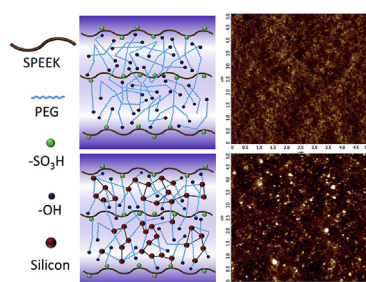
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HIGHLIGHTS

- SPEEK-PEG/SiO₂ cross-linked interpenetrating polymer network based membrane.
- Highest conductivity of SPEEK-PEG/SiO₂ (10%) is 0.185 S cm⁻¹ at 80 °C and 100% RH.
- Membrane has good form stability up to 80 °C in water.
- Tensile strength and % elongation in the range of 16–25 MPa and 150–240%.
- Maximum power density in H₂/O₂ fuel cell is 379 mW cm⁻², at 800 mA cm⁻² and 0.47 V.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Proton exchange membrane
Sulfonated poly(ether ether ketone)
Nanocomposite
Interpenetrating polymer network
Fuel-cell

ABSTRACT

A series of sulfonated poly(ether ether ketone)-poly(ethylene glycol) cross-linked interpenetrating polymer network/SiO₂ nanocomposite membranes are developed for fuel cell application. Poly(ethylene glycol) is used as cross-linker to induce interpenetrating polymer network structure, and simultaneously, acting as a dispersant to homogeneously distribute SiO₂ nanoparticles. The synergistic effect of cross-linking and inorganic additive on the membrane properties and on its performance in the fuel cell are investigated. Experimental results reveal that nanocomposite membrane have better properties than pristine sulfonated poly(ether ether ketone)-poly(ethylene glycol) membrane. Composite membrane with 10 wt% SiO₂ has the best membrane properties e.g. highest conductivity of 0.185 S cm⁻¹ at 80 °C and 100% relative humidity. The instrumental characterization shows that the SiO₂ nanoparticles are distributed homogeneously, and the average particle size is less than 70 nm. The membranes performance in fuel cell is increased more than twofold i.e. maximum power density of 170 mW cm⁻² at 460 mA cm⁻² and at 0.4 V for pristine membrane without SiO₂ which is enhanced to 379 mW cm⁻² at 800 mA cm⁻² and at 0.47 V for membrane with 10 wt% SiO₂. These results indicate that, this membrane has potential in fuel cell application.

1. Introduction

Fuel cell system is an advanced power system for the future that is

sustainable, clean and environment friendly. Proton exchange membrane fuel cells (PEMFCs), with the advantages of high power density and efficiency, low operating temperature, fast start-up, noiseless

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feature, static nature and safe handling are being developed as an alternative to conventional internal combustion engines, secondary batteries, and other power sources [1,2]. In the last few decades, much effort has been devoted to develop PEMFCs, and significant advancement has been achieved. However, their commercialization has not been achieved and the major problem is the prohibitive cost and durability of the component materials (membrane electrolyte, bipolar plate and Pt electro catalyst) [3–5].

One of the key components of PEMFCs is the polymer electrolyte membrane (PEM), which behaves as an electrolyte to conduct protons from the anode to the cathode and separates the reactant gasses. To date, the Perfluorinated sulfonic acid membranes (PFSA) like Nafion have been perceived as most suitable PEMs because of their high proton conductivity and stability [6]. However, their high cost, performance loss at higher temperatures (above 80 °C) or low humidity (below 80% RH), high fuel cross over etc., impedes the large scales commercialization of PEMFCs [7,8].

Aromatic hydrocarbon-based membranes are a promising alternative to PFSA membranes due to their low cost, good stability (thermal and mechanical), processability and wide latitude to tune the chemistry. During the last few decades, sulfonated poly(arylene ether ketone)s (SPAEEK) [9,10], sulfonated poly(imide) (SPI) [11], sulfonated poly(arylene ether sulfone)s (SPAES) [12,13], and acid-doped poly-benzimidazole (PBI) [14,15], etc. have been extensively studied by different research groups. Among the numerous hydrocarbon polymers, sulfonated poly(ether ether ketone) (SPEEK) is a good candidate on account of its low cost, high glass transition temperature and high proton conductivity, which depend on its degree of sulfonation (DS). SPEEK membranes with high DS exhibit high proton conductivity and ion exchange capacity value (IEC). Moreover, the large number of sulfonic acid groups also result in poor mechanical and dimensional stability, which is unfavorable for electrochemical applications [16]. In order to improve the mechanical and dimensional stability, many modifications have been carried out, like cross-linking [17,18], blending with other polymers [19], semi-interpenetrating polymer networks [20], addition of inorganic fillers etc. [21].

Cross-linking method is a simple and effective way to achieve the desired properties including proton conductivity and mechanical/chemical stability of the membrane. Cross-linking of sulfonated aromatic poly-hydrocarbons can be conveniently achieved through bridging the reactive sulfonic acid functions by appropriate moieties. A series of studies has been carried out by different research groups on the development of covalently and ionically cross-linked polyarylenes [22–26], and the advantages and disadvantages of such efforts have been elaborated. Another method of cross-linking of SPEEK through intra/interchain condensation of sulfonic acid functionalities, that is initiated simply by appropriate thermal treatment, was introduced by the authors of a US patent [27]. This method was further implemented by Mikhailenko. et al., using simple polyatomic alcohols (ethylene glycol, glycerol), as cross-linker in different solvent/solvent pairs [28]. Other groups also studied the effect of cross-linking on membrane properties by using different aliphatic, cyclic and aromatic diols [29,30]. The performance properties of SPEEK were found to be dependent on the nature of cross-linker and the best properties were obtained when ethylene glycol [EG] and poly ethylene glycol (PEG) were used as cross-linker. Recently our group, thoroughly studied the performance and properties of cross-linked SPEEK membranes by using different molecular weight of PEG as cross-linker and found that there is a significant effect of cross-linker chain length on membrane properties [31]. PEG of molecular weight 400 Da showed the appropriate chain length for better hydrophilic/hydrophobic phase separation and best electrochemical and mechanical properties. Although, cross-linking with PEG enhances the membrane properties to a great extent these membranes suffer from excessive swelling at a higher temperature in water.

Another effective approach has been reported to improve the

properties of PEMs by the incorporation of inorganic fillers into the organic polymer membranes (organic-inorganic nanocomposite/composite membranes). This is because of the combined influence of the organic and inorganic phases towards the thermal, mechanical, and chemical stability, as well as the electrochemical characteristics, in addition to the improved water retention property. During the last few decades, a number of efforts have been attempted by using different inorganic additives e.g., TiO_2 , SiO_2 , ZrO_2 , clay, heteropolyacids, zeolites etc. [32–39] to increase the performance of SPEEK based membranes. Among the numerous organic-inorganic composites, polymer/silica composites were extensively studied because of their lower cost, inferior electrical conductivity and better water retention properties etc. The homogenous distribution and minimizing the self-aggregation of inorganic additives in the polymer-inorganic composite membranes is the most important parameter that boosts the membrane properties. Among different methods of organic-inorganic composite membrane synthesis, the *in-situ* sol-gel method is the best approach to control the particle size and distribution of the inorganic phase into the polymer network. However, there is a compatibility issue between hydrocarbon polymer and silica which restricts the uniform distribution of silica particles into the polymer matrix and the composite membrane thus become opaque with the increase in silica content due to the rapid agglomeration of silica particles. Some research groups used synthetic surfactant e.g. urethane acrylate non-ionomer (UAN) to improve the compatibility between silica and poly(imide) and poly(styrene) based composite membranes [40,41].

The objective of this study was to prepare organic-inorganic nanocomposites in a combination of interpenetrating polymer network (IPN) type cross-linked structure to improve the electrochemical and mechanical properties of highly sulfonated SPEEK polymer based membrane. In this context, SPEEK-PEG/ SiO_2 membranes were fabricated where, PEG-400 is used as an IPN-type cross-linker as well as dispersant to homogeneously distribute silica nanoparticles which are synthesized by *in-situ* sol-gel method. Polyols (PEG) are highly beneficial for controlling inorganic particle nucleation, growth and agglomeration of nanoparticles as PEG adhere on the particle surface (especially on oxides) and serve as colloidal stabilizers [42].

In this work we have systematically investigated the effect of varying weight percentage of SiO_2 content (2.5, 5, 7.5, 10 and 12.5%) in the SPEEK-PEG/ SiO_2 nanocomposite membranes on different electrochemical and mechanical properties. The intermolecular structure and morphology of the SPEEK-PEG/ SiO_2 nanocomposite membranes were characterized by FT-IR, FESEM, AFM and EDX methods. The influence of SiO_2 addition has been discussed in terms of membranes conductivity, water uptake, chemical and mechanical stability and investigated the optimum concentration of SiO_2 . The membrane having optimum SiO_2 weight percentage, is studied in H_2/O_2 fuel cell and compared with pristine SPEEK-PEG membrane.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK) was purchased from Gharda chemicals (MW > 200000 Da), poly(ethylene glycol) (PEG) of molecular weight (400 Da) PEG-400 was purchased from Fluka Biochemical, sulphuric acid, ethanol were purchased from SD Fine chemicals (SDFCL) and are of analytical reagent (AR) grade. Tetraethyl orthosilicate purchased from sigma aldrich. Ethanol was distilled before use.

2.2. Sulfonation of Poly(ether ether ketone) (PEEK)

PEEK beads were dried in an oven at 100 °C overnight. Thereafter, 20 g of the PEEK was dissolved in 170 ml sulphuric acid and 30 ml methane sulfonic acid and vigorously stirred using a mechanical shaker at room temperature for 72 h. Then the sulfonated polymer solution

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