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SPEEK based Hybrid Proton Conducting Membrane for Fuel Cell Applications

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Abstract: *Expansion in energy requirement due to population growth and exhaustion of non-renewable energy has led to extensive research on renewable alternative energy sources. Fuel cells have the potential to provide alternative clean and green energy. In this research a novel and low cost methods has been initiated for the preparation of hybrid proton exchange membrane. PEEK polymers have been sulfonated using sulfuric acid and the degree of sulfonation of 67% is obtained using* ^{1}*H-NMR spectroscopy. The sulfonation of SPEEK polymer is identified by the new absorption bands at 1082 and 1224* cm^{-1} *due to stretching vibrations of the sulfonic acid group by FTIR spectroscopy. The electrolyte samples were prepared by solution casting technique using SPEEK and sulfonated* TiO_2*. The composite membranes exhibited improved mechanical strength and low water uptake. The hydrolytic stability of the membrane is studied by contact angle measurement. Addition of nanosized particles into the polymer electrolytes is better in improving the conductivity as well as mechanical properties of the membrane. The proton conductivity was enhanced by the introduction of hydrophilic inorganic particles into the SPEEK membranes, which might be an effective approach to increase the working temperature of the membrane. The conductivity value of the composite membrane is of the order of* 10^{-1} Scm^{-1} *at 70°C, observed under conditions of 100% humidity conditions. The prepared hybrid membranes offer great potential for use as proton exchange membrane in fuel cells.*

Keywords: *Proton conductivity, Contact angle, Mechanical stability*

I. INTRODUCTION

Oil, gas, coal and non-fossil fuels each satisfy around only a quarter of the world's energy requirement by 2040. More than 40% of the overall increase in energy demand is met by renewable energy". Power accounts for nearly 70% of the increase in primary energy demand. China and India account for half of the growth in global energy demand around 2040. India is going to overtake China as the world's fastest growing market for energy by the early 2030s and carbon emissions rise by 10% by 2040. **[**BP Energy Outlook 2018]. Fuel cells have various advantages over conventional power sources, such as internal combustion engines or batteries. Fuel cells are electrochemical devices in which the chemical energy of fuel is converted directly to electrical energy through an electro-catalytic process. This technology has been the focus of new energy technology development because of its noteworthy features. Greenhouse gases are eliminated over the whole cycle by the usage of fuel cells. The maintenance of fuel cells is simple since there are few moving parts in the system. The main part of the fuel cell is proton exchange membrane which is prepared by polymer electrolyte membrane [1]. Various aromatic polymers are used to prepare polymer electrolyte membrane, among them Polyetheretherketone (PEEK) is easily available having high thermal, mechanical and oxidative stability. Sulfonation of PEEK improves the hydrophilicity of the polymer which is favorable for protonic conductivity of the membrane. Addition of nano fillers, improves the efficiency of polymer electrolyte membrane and its stability [2]. Incorporating inorganic particles into SPEEK acts as a barrier for methanol crossover and increases the mechanical stability of the membrane due to the hydrogen bond formed between the $-SO_3H$ group from SPEEK and the –OH group from the inorganic particles

II. MATERIALS AND METHODS

PEEK (M_W= 20800) (Sigma Aldrich, USA), (DMSO) (Merck, Germany), (H_2SO_4 - 98%) (Merck, Germany), (TiO_2 - nanosize). The polymer electrolyte membranes are prepared by solution casting method.

PEEK polymer was completely dried in a vacuum oven at 100°C for 24 hours to remove the moisture prior to its use. The Sulfonated PEEK (SPEEK) was prepared by reaction of 5 g of PEEK with 100 ml concentrated sulfuric acid at 50°C for 2 hours. The polymer is completely dissolved in 1 hour and the reaction was continued for further 5 hours at a temperature of 45°C. The resultant mixture was poured into ice-cold deionized water to precipitate the sulfonated polymer (SPEEK) under continuous agitation and it was left overnight [3]. The precipitated form of SPEEK was washed with deionized water for several times until pH becomes neutral, dried under room temperature overnight and was further dried in vacuum oven at 80°C for 24 hours. The sulfonated TiO_2 was prepared by adding 0.5g of TiO_2 in 10ml of 0.3M sulfuric acid under ultrasonication for 1 h [4]. The sulfonated titania (S-TiO_2) powder was obtained by drying at 70°C for 9 hours.

To prepare the polymer composite membranes, SPEEK was completely dissolved in DMSO at room temperature. With this solution 2wt % of TiO_2 and S-TiO_2 are added separately and the solution was stirred continuously for 8 hours to properly disperse the nano particle and cast on a glass plate. The cast membranes were dried at 70°C for 8 hours. After being cooled down to room temperature, the membranes were peeled off from the glass plate and the thickness of the membrane is in the range of 0.08 – 0.11 mm.

The functional groups present in the membranes were recorded between 4000-400 cm^{-1} in transmittance mode at a resolution of about 4 cm^{-1} using Perkin Elmer FTIR spectrophotometer. Hydrophilic nature of the membrane are known from the Contact angle Goniometer (Rame-Hart 500, USA). Mechanical stability was studied by UTM- INSTRON – 3345, UK, at a speed of 10mm/min. and Proton conductivity of the membrane were investigated over the frequency range of 10 Hz to 10 MHz with 5 mV oscillating voltage using frequency response analyzer (FRA) (HI604D) .

III. RESULT AND DISCUSSION

3.1. Functional group analysis – FTIR

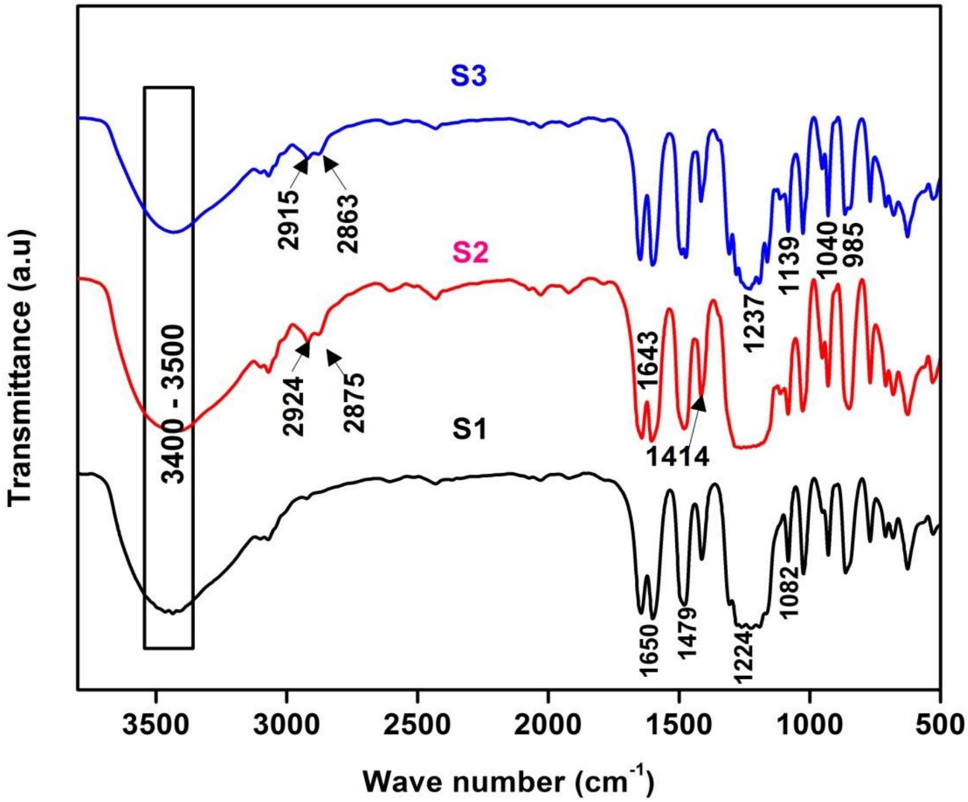

Figure 1. FTIR spectra of SPEEK(S1), SPEEK-TiO_2(S2), SPEEK-S TiO_2 (S3)

FTIR spectroscopy is a very important tool for the investigation of functional group of polymer structures, shown in Fig. 1. The new absorption bands at 1082 and 1224 cm^{-1} of SPEEK identify the symmetric and asymmetric stretching vibrations of the sulfonic acid group. The aromatic C–C band at 1485 cm^{-1} and the peak at 1650 cm^{-1} corresponds to the stretching of carbonyl groups. The peaks below 700 cm^{-1} were assigned to the stretching vibration of Ti-O and Ti-O-Ti groups in titania nanoparticles. The symmetrical and asymmetrical vibrations of -CH_2 groups and also the bending vibration of C-H groups were observed at 2854, 2923 and 1461 cm^{-1}[5]. The bands at 3400 cm^{-1} and 1634 cm^{-1} are attributed to the -OH stretching and H-O-H bending vibrations, clearly demonstrate the water- retention of SPEEK and composite membranes. This confirmed the strong interaction between the polymer matrix and nano filler[6]. The band at 1040 cm^{-1}, 985 cm^{-1} is assigned to the asymmetric stretching vibration of S-O groups, whereas the bands at 1139 and 1237 cm^{-1} are attributed to the splitting of the S-O group into symmetric and asymmetric stretching vibrations of sulfonated titania [7]. The spectra also exhibited the bands at 1011 cm^{-1} and 1089 cm^{-1} associated with the hydrogen bonding of Ti-O with sulfonyl of SPEEK [3,4] . In all spectra, aromatic groups from PEEK backbone and sulfonic acid groups are observed [2]. The above analysis establishes the formation composite membranes.

3.2. Contact angle measurement

Contact angle measurements confirmed the hydrophilicity/ hydrophobicity of the polymer composite surface and water flux was measured to evaluate the permeation property of the membranes. The static water contact angles for all of the samples had been evaluated, as shown in Fig. 2. The water contact angles distinctly depended on the contacting time between the membrane and water, and the angles decreased with the time. The contact angle value of the SPEEK-TiO2 membrane is higher than pristine SPEEK membrane due to hydrophobic nature of nano filler [8,9]. A decrease in contact angle of the SPEEK/S-TiO_2 composite membrane implies that the surface becomes more polar by the addition of sulfonated nano filler. All membranes show contact angle value below 90°, indicate that all membranes were hydrophilic in nature due to the presence of the sulfonic acid functional group in the SPEEK polymer chain.

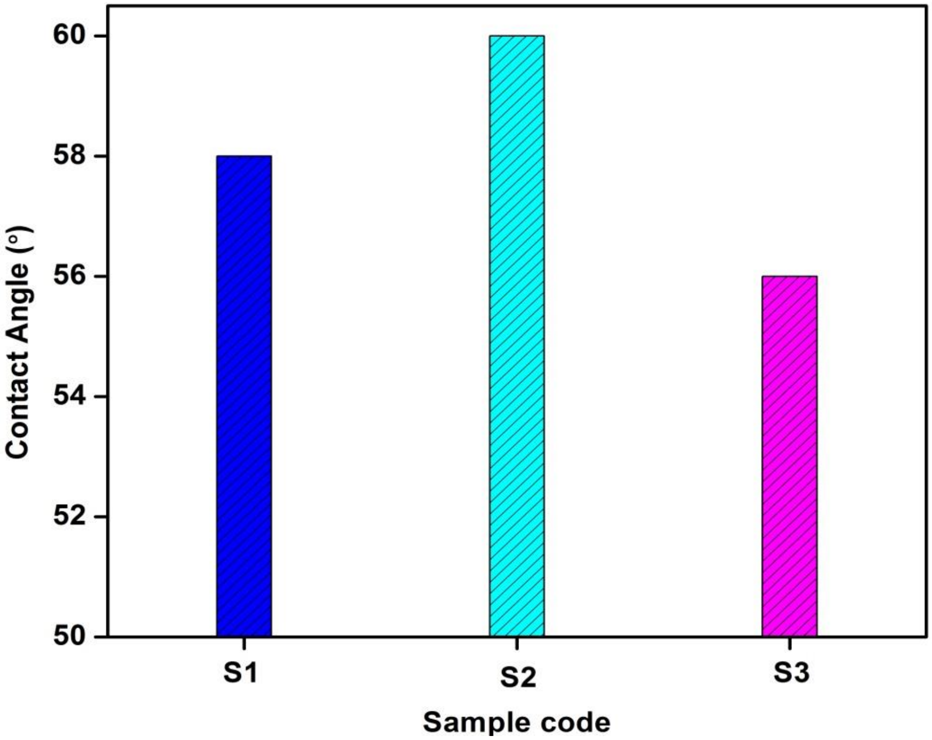

Figure 2. Contact angle of composite membranes

3.3. Mechanical property

Adequate mechanical strengths are required for PEMS to guarantee a long life time for the fuel cell application. The mechanical properties of SPEEK and hybrid membranes are studied at room temperature in dry state and are shown in Table1. Incorporation of TiO_2 nano fillers enhances the mechanical stability of the polymer electrolytes hence enhances methanol barrier properties. Due to the hydrophobicity of the TiO_2 fillers, the structural changes are induced which could restrict the polymer chain segmental mobility and enhances the rigidity of resultant hybrid membranes [10]. The degree of elongation for the hybrid membranes were remarkably decreased to about 92% while the Young's Modulus is increased [11]. The increase in Young's modulus could be also attributed to increased chain rigidity imparted by the improved polymer - filler interactions. The sulfonated titania reduces the stiffness of the polymer back bone hence percentage of elongation is increased. Therefore, hybrid membranes showed improved mechanical properties than pristine SPEEK membrane and are adequate to meet the requirement for the operation of fuel cells [3].

Table 1. Mechanical properties of composite membranes

Sample Code	Composition (wt%)	Young's Modulus (MPa)	Elongation (%)	Water Uptake(%)
S1	SPEEK	7.37	38.74	33
S2	SPEEK/TiO_2 (2wt%)	8.55	35.67	28
S3	SPEEK/S-TiO_2 (2wt%)	4.97	39.07	32

3.4. Proton conductivity

Proton conductivity is an essential parameter for evaluating the polymer electrolyte membrane's performance. The measurement of proton conductivity was carried out in the temperature range of 30°C to 70°C as shown in Fig.3. It can be observed that proton conductivity decreases with the addition of inorganic filler due to reduction in sulfonic acid group. However, lower water uptake content in composite membranes decreases methanol crossover which is favorable for fuel cell operation [12]. The conductivity of the composite membranes with sulfonated titania (S-TiO_2) was superior to that of SPEEK and SPEEK-TiO_2 membranes. This was ascribed to the hygroscopic properties of sulfonated nanoparticles, their suitable dispersion in polymer matrix and channeling of water molecules facilitated the proton transfer through the membrane. An additional proton conduction pathway was created due to molecular water absorption by S-TiO_2 [4,5]. As the temperature increases the charge carries are thermally activated and the free volume increases and more vacant sites are created for the motion of ions, which in turn enhances the conductivity.

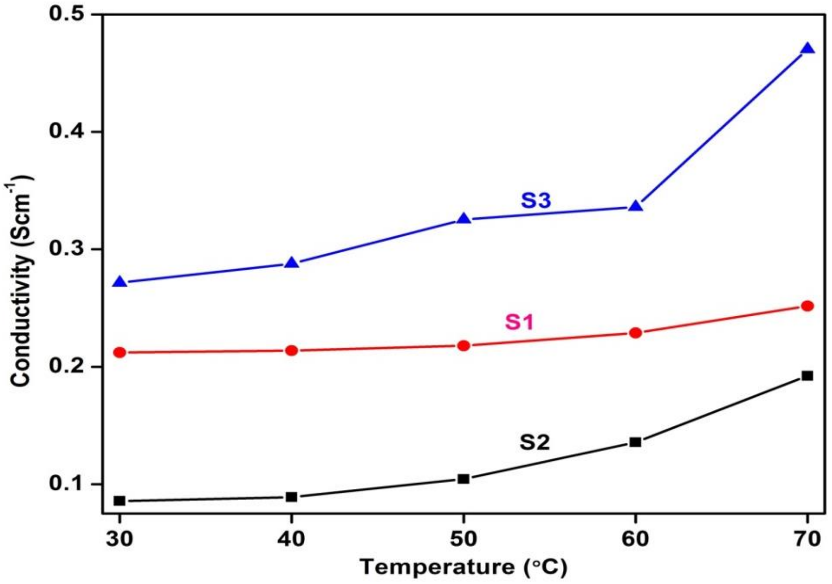

Figure 3. Proton conductivity of composite membrane

IV. CONCLUSION

In the present work we have studied composites of SPEEK with hydrophobic and hydrophilic TiO_2. The influence of the fillers on the properties and performances of SPEEK membranes were extensively characterized by FTIR, contact angle, mechanical test and proton conductivity. The composites with hydrophobic TiO_2 presents relatively low proton conductivity due to blocking effect of nanofiller. The addition of 2 wt% of TiO_2 has a beneficial effect on the mechanical properties of the electrolyte membrane. The addition S-TiO_2 strengthened the interactions and improved the interfacial compatibility between the inorganic filler and the polymer matrix. The SPEEK/S-TiO_2 hybrid membranes displayed higher proton conductivity in comparison with the pristine SPEEK membrane and the SPEEK/TiO_2 membrane. The maximum proton conductivity value was found to be 4.3×10^{-1} Scm^{-1} at 70°C for 2wt% sulfonated Titania. The hydrophilic nature promotes the ion channels and swells the membrane which results in the enhancement of proton conductivity. The above results suggest a potential application of this kind of solid polymer electrolyte in fuel cells.

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