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**Polyaniline coated sulfonated TiO₂ nanoparticles for effective application in proton
conductive polymer membrane fuel cell**

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ABSTRACT

The sulfonated polyethersulfone (SPES) with modified TiO₂ proton exchange membrane performance for the fuel cell application was reported. TiO₂ nanoparticles investigated for the fuel cell performance were modified by sulfonation and surface coated using polyaniline (PANI). Fabricated membranes were analyzed in terms of water uptake, swelling ratio, methanol uptake, ion exchange capacity, chemical stability and thermal properties. Surface and structural properties of the membranes were characterized by Field Emission Scanning electron microscope (FESEM). To understand the interaction between polymer and nanoparticle, Fourier transform infrared (FTIR) and X-ray diffraction (XRD) characterization for the membranes were performed. Highest proton conductivity is 2.30×10^{-4} S/cm with SPES/STiO₂-PANI (0.5%) composite membrane. The presence of modified TiO₂ with amine group of PANI and sulfonic acid group were the main factors for the highest conductivity value. The composite membrane with modified TiO₂ shows excellent chemical stability and thermal properties. Thus, the composite membrane incorporated with STiO₂-PANI is a promising proton conducting material for fuel cell application.

Keywords: Sulfonated polyethersulfone; Surface modified TiO₂; Emeraldine part of PANI; Proton exchange membrane; Conductivity.

1. Introduction

The fuel cell is a device which converts fuel into electricity and water through electrochemical reactions. High efficiency and eco-friendly technology with low emission of greenhouse gases invade fuel cell to be a promising alternative clean energy resource [1, 2]. Proton exchange membrane fuel cell (PEMFC) utilizes methanol or hydrogen for an automotive application as a clean energy source [3]. The efficiency of the fuel cell system mainly depends on the performance of the Proton exchange membrane (PEM) [4]. An ideal PEM should possess excellent conductivity at an affordable price [5]. For the past few years, perfluorosulfonate polymer Nafion was used as PEM in fuel cell system for its excellent proton conductivity [6, 7]. Even though it exhibits this quality, high expenditure on the material, high fuel crossover, low proton conductivity at high temperature and poor mechanical strength under hydrated condition are the negative aspects of Nafion [8]. These challenges hinder the commercialization of the fuel cell to a larger extent and thus it provokes the need for synthesis of alternative membrane material. The alternative membrane material should possess low fuel crossover, high performance and high conductivity at low cost than Nafion [9].

In fuel cell technology, two types of materials have been used as PEM. The first is the usage of organic polymer material alone which exhibits excellent chemical and thermal stability at low cost [10]. The aromatic polymers used as an alternative membrane material are polyimide, polybenzimidazole, poly(ether ether ketone), polysulfones, polyetherketones and polyethersulfone [11]. These materials were used as PEM after sulfonation method. The second kind is the use of an organic and inorganic material as components to synthesis the polymer composite membrane which exhibits the synergistic properties of both the materials. SiO_2 , TiO_2 ,

69 ZrO_2 , Al_2O_3 , MMT, etc were used as an inorganic material for the preparation of composite
70 membranes [12].

71 Researchers have shown more attention towards thermoplastic polyethersulfone (PES) polymer
72 which has repeated phenyl and sulfone groups. PES exhibits excellent chemical, thermal and
73 mechanical properties [13]. Even though PES has unique physical properties, low proton
74 conductivity of this polymer drags the application in PEMFC. Sulfonation of PES is one of the
75 methods to make it suitable for fuel cell application [14, 15]. The unique properties, easy and low
76 cost of synthesis have attracted the hydrocarbon-based sulfonated PES as a promising material in
77 PEMFC [16]. Recently, the properties of SPES membrane have been improved by impregnating
78 nanoparticle within the polymeric chain [17].

79 Pure conductivity polymers are chemically and mechanically unstable. For this reason, titanium
80 dioxide (TiO_2) and conducting polymer (PANI) are hybridized. Hygroscopic nature, high surface
81 area, photocatalytic and photoelectric conversion of TiO_2 nanoparticle have attracted the
82 scientists to use it in various fields [18]. Sulfonation of TiO_2 would increase the hydrophilic
83 nature of TiO_2 and improves the ability to absorb more water molecules which might provide the
84 path for transport of protons [19].

85 Some interesting semiconducting polymers are phenylenediamines, alkoxyaniline, halogenated
86 anilines, aminophenols, aminobenzenesulfonic acid, aminopyrene, diphenylamines, 1-amino-2-
87 pyridine, N-alkylaniline, N,N-dimethylaniline and N-phenylaniline [20]. Polyaniline (PANI) is
88 the polymeric product of aniline prepared under acidic condition. The conductive nature, easy of
89 synthesis, low cost for synthesis and environmental stability attracts PANI to be an effective
90 material for fuel cell application [21–24]. Among conducting polymers, PANI is the cheapest
91 material exhibits good conductivity [25]. Many researchers have studied the synthesis and

characterization of TiO_2 –PANI composite membrane for various applications [26–29]. There is no proper research work on synthesis and characterization of STiO_2 –PANI composite membrane for fuel cell application.

In this work, the sulfonated polyethersulfone (SPES) was used as organic polymer phase. The inorganic material (STiO_2 and STiO_2 –PANI nanocomposite) were synthesized and characterized by FTIR and XRD. The composite membranes were prepared by incorporating the inorganic materials within the polymeric phase individually at 0.5 and 1% loading rate.

2. Experimental

2.1. Materials

Polyethersulfone (PES) was purchased from RADEL A-300, Amoco Chemicals (Atlanta, GA). Aniline and ammonium persulfate (APS) were procured from Finar Limited (India). Merck (India) have provided sodium chloride (NaCl), sodium hydroxide (NaOH), phenolphthalein 1%, N-methyl-2-pyrrolidone (NMP) and hydrogen peroxide (H_2O_2) 30%. Ammonium ferrous sulphate was purchased from Loba Chemie Pvt. Ltd., India. Sulfuric acid (H_2SO_4) 98% was supplied by Thermo Fisher Scientific (India). Hydrochloric acid (HCl) 35% was obtained from Merck life science private limited, India. TiO_2 nanoparticle was supplied by Sigma Aldrich.

2.2. Preparation of STiO_2

The methodology followed for the preparation of STiO_2 was reported in Zhimou et al. [19]. 1g of TiO_2 nanoparticle was dispersed in 15 ml of 0.5 M H_2SO_4 at room temperature. After 8 h of continuous stirring for sulfonation process, the solution was filtered, rinsed by deionized water and dried at 90 °C. The obtained powder was calcined at 500 °C for 3 h to obtain sulfonated TiO_2 (STiO_2).

2.3. Preparation of STiO_2 –PANI nanocomposite

The methodology followed for the preparation of STiO₂-PANI nanocomposite was reported in Xingwei et al. [28]. 1ml of aniline was added to 80 ml of 2 M HCl solution containing 1g of STiO₂ nanoparticle. After 10 h of continuous stirring, few drops of 5% FeSO₄ solution was added. Ammonium persulfate (APS) solution was prepared by dissolving 1g of Ammonium persulfate in 20 ml of distilled water. APS solution was added in drop wise under continuous stirring. The solution was allowed to polymerize at room temperature for 5 h. The polymerized solution was filtered, washed by 2 M HCl and deionized water for several times. After drying in an oven at 60 °C, green powder of STiO₂-PANI nanocomposite was obtained. The schematic representation of polyaniline coated sulfonated TiO₂ is shown in Fig. 1. Three interactions such as hydrogen bonding, coordinate bonding, electrostatic interactions and sorption interaction are there at the STiO₂-PANI interfaces. Hydrogen bonding may be formed between aniline NH₂ group and hydroxide group of the STiO₂. Coordinate bonding might be formed between the NH₂ group of PANI and Ti atom of STiO₂. Aniline monomers react with HCl to form anilinium chloride and there is an electrostatic interaction between the surface of STiO₂ nanoparticles and anilinium chloride. APS was used as an oxidizing agent whom oxidizes and polymerize aniline. While polymerization the molecular weight of the polymer increases and their solubility in water gets decreased. As a result of this, the polymer gets deposited, adsorbed and coated over the surface of STiO₂ nanoparticles to form STiO₂-PANI nanocomposite [18].

2.4. Preparation and characterization of SPES

200 ml of concentrated sulfuric acid is used to dissolve 20 g of PES polymer and stirred vigorously until the solution becomes homogeneous. After 15 h of reaction time, the solution was poured into the ice cold water bath under continuous agitation to cease the sulfonation reaction. The SPES was filtered and washed with deionized water for several times until the pH

becomes neutral (pH=7). Further, sulfonated polyethersulfone (SPES) was dried at 80 °C for overnight. The presence of sulfonation group within the sulfonated polymer (SPES) backbone was determined by ¹H-NMR spectroscopy (Bruker Instrument, Germany).

2.5. Preparation of polymer membranes

The polymer composite membranes were fabricated by phase inversion technique using N-methyl-2-pyrrolidone (NMP) as a solvent. The synthesized STiO₂ and STiO₂-PANI nanocomposite were dissolved individually in NMP solvent at the loading rate of 0.5% and 1%. The compositions of the fabricated membranes were listed in Table 1. To the casting solutions, SPES was added and stirred at 50 °C. After getting homogeneous mixture, the casting solutions were kept aside for the removal of dissolved air bubbles and the solutions were casted onto a glass plate using casting knife. For the removal of trapped solvent within the membrane, the glass plates were dried for 12 h at 70 °C. The membranes were detached from the glass and stored for further study.

2.6. Characterizations

FTIR and XRD analysis were performed for the prepared STiO₂ and STiO₂-PANI nanocomposite. FESEM is useful to study the morphology and distribution of nanoparticle within the polymer composite membrane. The gold sputter coated membrane was used for FESEM analysis (Carl Zeiss, UK). To study the functional group, FTIR for the membrane was recorded using Perkin Elmer/Spectrum 2, USA. XRD pattern for the membrane was analyzed from 5 ° to 90 ° at 2θ angle using PANalytical X'Pert Pro (Cu-Kα radiation).

2.7. Water uptake

The dried membrane weight was noted and soaked in deionized water at room temperature for overnight. The wet membrane was wiped with tissue paper and the wet weight was noted. Water content was measured using the following equation.

$$\text{Water Uptake (\%)} = \frac{(W - D)}{D} \times 100 \quad (1)$$

where W is the wet mass of the membrane and D is the dry mass of the membrane respectively.

2.8. Methanol uptake

The methanol uptake was studied by immersing the membrane in methanol for 24 h. Prior to measuring the wet weight, the membrane was wiped with tissue paper. After drying in an oven for 24 h at 80 °C, the dry weight was recorded. The methanol uptake was determined from the equation below.

$$\text{Methanol Uptake (\%)} = \frac{(\text{Wet weight} - \text{Dry weight})}{\text{Dry weight}} \times 100 \quad (2)$$

2.9. Swelling ratio

The geometrical area of the membrane under hydrated (water) and dried conditions were recorded. The swelling ratio at room temperature was calculated as

$$\text{Swelling ratio(\%)} = \frac{(\text{Wet membrane Area} - \text{Dry membrane Area})}{\text{Dry membrane Area}} \times 100 \quad (3)$$

2.10. Ion Exchange Capacity (IEC)

The dry membrane was soaked in 1 M NaCl for 24 h and it swaps the H⁺ ions in the membrane to Na⁺ ions. The solution was neutralized with 0.012M of NaOH and phenolphthalein was used as an indicator. From the titrated value, the IEC was measured by the given equation.

$$\text{Ion exchange capacity} \left(\frac{\text{meq}}{\text{g}} \right) = \frac{\text{Volume} \times \text{Normality}}{D} \quad (4)$$

where D is the dry mass of the membrane (g).

2.11. Chemical stability

Fenton test is used to determine the chemical or oxidative stability of the membrane and it was determined by soaking the dry membrane in 3% of H₂O₂ aqueous solution at 68 °C. Under continuous stirring 4 ppm of ammonium ferrous sulphate was added. After fixed intervals of time, the membrane was removed from the solution and rinsed with water. The residual weight of the membrane was determined.

2.12. Differential scanning calorimetry (DSC)

Thermal property of the membrane was analyzed by Differential scanning calorimetry (DSC 6000–Perklin Elmer). The thermogram of the membrane was recorded under a nitrogen atmosphere between 20 °C and 350 °C which was scanned at a heating rate of 10 °C min⁻¹.

2.13. Proton conductivity

The resistance of the membrane was recorded over the frequency range between 1 MHz and 50 Hz with the amplitude of 10 mV using potentiostat (Bio–logic VMP3, France). Prior to analysis, membrane was soaked in deionized water for overnight. The conductivity measurement cell with stainless steel electrodes would hold the membrane. The conductivity of the membrane was calculated by the equation below.

$$\text{Proton Conductivity (S/cm)} = \frac{d}{R \times S} \quad (5)$$

where d is the thickness of the membrane, R is the resistance and S is the surface area of the electrode respectively.

3. Results and discussion

3.1. Confirmation of sulfonation using NMR spectroscopy

The structure of PES and SPES were characterized by ¹H–NMR spectroscopy and shown in Fig. 2. The spectrum for PES shown peaks at 7.3 and 8.0 were corresponds to the phenyl group

present in the polymeric chain. For SPES, the down-field shift from 8.0 to 8.1 ppm of the hydrogen (H) located in the ortho position at the aromatic ring confirms the presence of sulfonic acid groups within the polymeric chain [30]. The appearance of new peaks in the SPES spectrum also revealed that sulfonation was occurred in the PES polymer [31]. The introduction of sulfonic acid groups could have a significant effect on the membrane properties such as IEC and proton conductivity [32].

3.2. Confirmation of functional group in nanoparticles and membranes using FTIR

The functional group of modified TiO_2 nanoparticle was analyzed by FTIR and the spectra are shown in Fig. 3. For STiO_2 , the spectrum was wide, broad and there is no significant peak. Since during the synthesis of STiO_2 , the nanoparticle was calcined at high temperature (500°C) reported by Zhimou et al. [19] which might reduces the peak intensity. However, the XRD pattern for STiO_2 nanoparticle shown peak at 2θ of 25.3° which confirms the sulfonation of TiO_2 nanoparticle which is in accordance with the XRD result of Zhimou et al. and it was explained in section 3.3. Thus the spectra appeared to be broad. The spectra for STiO_2 have confirmed the sulfonation of TiO_2 nanoparticle. For STiO_2 -PANI nanocomposite, an N-H stretching spectrum occurs at 3447 cm^{-1} . At 1581 cm^{-1} , the spectra corresponds to C=N of quinonoid ring and peak at 1481 cm^{-1} corresponds to C=C benzenoid ring stretching. C-N stretching of benzenoid ring spectra occurs at 1290 cm^{-1} . The characteristic band detected at 1121 cm^{-1} corresponds to quinonoid unit of PANI [18]. The broad band at 503 cm^{-1} attributed to Ti-O. For STiO_2 -PANI nanocomposite, the spectra have confirmed that the presence of both STiO_2 and conducting emeraldine part of PANI. When Compared to STiO_2 , new peaks were appeared in STiO_2 -PANI nanocomposite which represents the strong interaction between PANI and STiO_2 [25].

Fig. 4 shows the spectra of SPES composite membranes. All membranes exhibit spectra at 1235 cm^{-1} are assigned to C–O–C stretching of PES. The stretching of sulfonate group for SPES and composite membranes are revealed at 1088 cm^{-1} [33]. The peaks at $1,230\text{ cm}^{-1}$ and 1088 cm^{-1} represents the asymmetric O=S=O and symmetric O=S=O stretching vibrations. These peaks in SPES and composite membranes confirm the presence of sulfonic acid group [34].

3.3. XRD analysis for synthesized nanoparticles and membranes

XRD patterns for STiO₂ and STiO₂–PANI nanocomposite are shown in Fig. 5. For STiO₂, the significant peak at $2\theta=25.3^\circ$ shows the crystallographic nature and using Debye–Scherrer’s equation, the crystallite size of STiO₂ was found as 8.1nm [19]. The peaks at $2\theta= 27.4^\circ, 37.8^\circ, 47.9^\circ, 54^\circ, 62.6^\circ$ and 68.9° for STiO₂ shows the characteristic peaks of crystalline TiO₂. For STiO₂–PANI nanocomposite, the highest peak appeared at 2θ of 20.3° is for PANI. The interaction between PANI and STiO₂ has decreased the crystalline nature. When the deposited PANI was absorbed on the STiO₂ surface, the interaction between PANI and STiO₂ restrict the formation of the polymeric chain around STiO₂ nanoparticle [25]. Thus, the crystalline nature of PANI is hindered and reduces the degree of crystallinity [28]. The XRD pattern of STiO₂–PANI nanocomposite shows the characteristic peaks of both STiO₂ and PANI [22]. The spectra also represent the ordered arrangement of PANI in the nanocomposite [29].

Fig. 6 shows the diffraction patterns of SPES composite membranes. For all the membranes, the broad band at 2θ of 10° and 20° represents the amorphous nature of base SPES polymer which is arisen from the hydrophilic sulfonic acid group [33]. The composite membranes exhibit peak at 2θ value of 18° beside this value show weak peak.

3.4. Surface morphology of membranes

FESEM image of SPES composite membranes are shown in Fig. 7. The surface morphology of the composite membranes represents the interaction between nanoparticles (STiO₂ and STiO₂-PANI) and polymer matrix. The membranes were appeared to be homogeneous with nonporous structure. The nonporous structure of the membrane is formed by the dry phase inversion technique. During fabrication, the slow movement of solvent from the membrane creates non porous structure. The transport of proton through PEM is governed by morphology of the membrane. The dense membrane is suitable for fuel cell application because it retard the movement of substrate and promotes the movement of protons. In SPES/STiO₂-PANI composite membrane, the added STiO₂-PANI nanocomposite was tightly bound to the polymer chain.

3.5. Water uptake and swelling ratio

Water uptake is a vital requirement for PEM because it aids the transfer of proton through the membrane [35]. The water uptake for SPES composite membranes are given in Table 2. The highest value is 7.18% with STiO₂-PANI (1%) compared to all the membranes. Hygroscopic nature of added STiO₂-PANI and the bonding between OH group of STiO₂ and water molecules acts as a vehicle to accommodate water molecules. This facilitates the membrane to imbibe more water molecules which helps to enhance proton conductivity [36]. The water uptake value increased when the loading rate of STiO₂-PANI has increased from 0.5 to 1%. Since the increased loading of STiO₂-PANI increases the hydrophilic region of the membrane matrix. The difference in the water uptake value is also due to the morphology of the membrane which has its influence on the interconnections of ionic cluster responsible for water absorption [34].

The swelling ratio of the membranes was less than 1% for all the membranes and exhibits good stability with negligible swelling. Since the mobility of the polymeric chain is hindered by the added nanoparticle which decreases the swelling properties.

3.6. Methanol uptake

Table 3 shows the percentage of methanol uptake of SPES and composite membranes. Methanol uptake (2M) was slightly greater than the water uptake for all the membranes except SPES/STiO₂ (0.5%) and SPES/STiO₂–PANI (0.5%) membranes. This result indicates that the SPES/STiO₂ (0.5%) and SPES/STiO₂–PANI (0.5%) membranes exhibits lesser attraction for the methanol than the water. While the lack of interaction between the ionic moieties present in the membrane matrix and methanol reduces the methanol uptake. In addition, the cross-linking between the emeraldine part of PANI and sulfonic group in the membrane matrix might be the reason for the observed behavior at low methanol concentration [21]. For pure methanol, the methanol uptake of all the membranes were found to be highest than the 2 M and 5 M methanol uptake. Since the sulfonation groups within the membrane matrix have greater attraction towards methanol [2].

3.7. Ion Exchange Capacity

The IEC of SPES and composite membranes are listed in Table 2. The IEC value decreases in the order of SPES/STiO₂–PANI (0.5%) > SPES/ STiO₂ (1%) > SPES/STiO₂ (0.5%) > SPES > SPES/ STiO₂–PANI (1%). The IEC value of SPES/ STiO₂–PANI (0.5%) is highest when compared with all the membranes. The result states that the presences of sulfonic acid groups provide by added STiO₂–PANI is responsible for ion exchange. The IEC value depends on the presence of sulfonic group within the polymeric matrix and makes positive effects on proton conductivity [33]. There was a negative impact on IEC when STiO₂–PANI loading was

increased from 0.5% to 1%. This is because of the development of secondary amine groups, neutralization or counteract of sulfonic groups, compact structure and the formation of hydrogen bond with the sulfonated membrane matrix [21, 37].

3.8. Chemical stability

Membrane stability in Fenton's reagent (oxidative environment) is an important factor to evaluate the PEM performance for fuel cell application. In PEMFC, the hydroxyl and hydroperoxy radicals generated are effective to attack membrane. These free radicals were generated during the decomposition of H_2O_2 catalyzed by ions and iron [38, 39]. The composite membranes were found to be stable in the Fenton's reagent for the fixed intervals of time.

3.9. Glass transition temperature (T_g)

The thermogram pattern of SPES composite membranes are shown in Fig. 8. T_g values were 234, 250, 246, 263 and 251 °C for SPES, SPES/ $STiO_2$ (0.5%), SPES/ $STiO_2$ (1%), SPES/ $STiO_2$ -PANI (0.5%) and SPES/ $STiO_2$ -PANI (1%) membranes respectively. In the composite membrane, the hydroxyl groups provide by added nanoparticles are interconnected by hydrogen bonding was responsible for high T_g . Additionally, the sulfonic acid group interaction also hinder the mobility of the polymeric chain and it shift the T_g to higher value [40]. From the thermogram, T_g was found to be greater than 250 °C which is higher than the normal operating temperature of PEMFC. Highest T_g is desirable for application of PEM in fuel cell system that gives the assurance for good thermal and dimensional stability intended for working under fuel cell operating conditions [41].

3.10. Proton conductivity

Table 2 shows the proton conductivity of SPES and composite membranes. The highest value is 2.30×10^{-4} S/cm with SPES/ $STiO_2$ -PANI (0.5%) membrane. The high proton

conductivity might be owing to the substantial affinity of hydrophilic region towards water. The amine groups of PANI provide by added STiO₂-PANI and the presence of sulfonic acid group contributes to form hydrophilic region in the membrane. Since it is responsible to hold water molecules for interconnecting the ionic domains within the polymer matrix and helps to transfer the proton [42, 43]. Additionally, the amine group of PANI (STiO₂-PANI nanocomposite) may form cross linking with the -SO₃H of SPES membrane matrix which hydrate the hydrophilic groups. The water molecules assist in proton movement and thus contributed to conductivity by water hopping mechanism [36]. But, on increasing the loading rate of STiO₂-PANI from 0.5 to 1% has a negative impact on conductivity value owing to the reduction of IEC. Significant/high proton conductivity is the vital factor required by the membrane to act as a proton exchanger. Low proton conductivity expressed by other membranes was due to the segregation of ionic domain within the polymeric structure.

4. Conclusions

Surface modified TiO₂ (STiO₂ and STiO₂-PANI nanocomposite) were synthesized and characterized by FTIR and XRD. Sulfonation of PES was also carried out and studied by ¹H-NMR spectroscopy. The highest proton conductivity value is 2.30×10⁻⁴ S/cm exhibited by SPES/STiO₂-PANI (0.5%) composite membrane. STiO₂-PANI in the polymer matrix enhanced ion exchange capacity due to presence of sulfonic acid group and amine group. The ionic domains present within the membrane were interconnected by the movement of water which influences the conductivity value. In addition to this, the SPES/STiO₂-PANI (0.5%) composite membrane also exhibit better fuel cell properties than the pristine SPES membrane. On increasing the loading rate of STiO₂-PANI nanocomposite from 0.5% to 1% have a negative impact on proton conductivity value. Since the reduction of IEC lessen the proton transfer and

thereby reduces proton conductivity. The effect of STiO₂–PANI nanocomposite on the PEM was found to be suitable with good conductivity property than the pristine SPES membrane and it would be a promising conductive material for the preparation of composite membrane in the fuel cell application.

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466   **Table captions**

467   **Table 1**

468   Composition of the fabricated membranes.

469   **Table 2**

470   Thickness, Water uptake, IEC and conductivity of the membranes.

471   **Table 3**

472   Methanol uptake of the polymer membranes.

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Table 1

Composition of the fabricated membranes.

Membrane Name	Modified TiO ₂ (g)	SPES (g)	Solvent (ml)
SPES	-	3.2708	15
SPES/STiO ₂ (0.5%)	0.0164	3.2544	15
SPES/ STiO ₂ (1%)	0.0327	3.2381	15
SPES/STiO ₂ –PANI (0.5%)	0.0164	3.2544	15
SPES/ STiO ₂ –PANI (1%)	0.0327	3.2381	15

496 **Table 2**

497 Thickness, Water uptake, IEC and conductivity of the membranes.

Membrane Name	Thickness (cm)	Water uptake (%)	IEC (meq/g)	Proton Conductivity (S/cm)
SPES	0.0061	3.47(0.59)	0.67(0.04)	2.32×10^{-5} (0.28)
SPES/STiO ₂ (0.5%)	0.0058	3.70(0.26)	0.69(0.03)	2.81×10^{-5} (0.22)
SPES/ STiO ₂ (1%)	0.0059	2.48(0.50)	0.72(0.05)	5.74×10^{-5} (0.26)
SPES/STiO ₂ –PANI (0.5%)	0.0058	4.54(0.44)	0.80(0.03)	2.30×10^{-4} (0.32)
SPES/ STiO ₂ –PANI (1%)	0.0058	7.18(0.40)	0.50(0.01)	5.16×10^{-5} (0.36)

498 (Values in parentheses are standard deviation).

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511 **Table 3**

512 Methanol uptake of the polymer membranes.

Methanol uptake (%)			
Membrane	2 M Methanol	5 M Methanol	Pure Methanol
SPES	5.26	4.17	13.83
SPES/STiO ₂ (0.5%)	1.74	4.35	14.66
SPES/ STiO ₂ (1%)	2.59	12.96	12.06
SPES/STiO ₂ –PANI (0.5%)	3.34	5.40	16.39
SPES/ STiO ₂ –PANI (1%)	8.23	6.98	18.82

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Figure captions

Fig. 1. Schematic representation of Polyaniline coated sulfonated TiO₂ nanoparticles

Fig. 2. ¹H–NMR spectra of PES and SPES.

Fig. 3. FTIR spectra of TiO₂, STiO₂ and STiO₂–PANI.

Fig. 4. FTIR spectra of pristine SPES and SPES composite membranes.

Fig. 5. XRD pattern of STiO₂ and STiO₂–PANI.

Fig. 6. XRD pattern of pristine SPES and SPES composite membranes.

Fig. 7. FESEM images of the membranes (a) SPES, (b) SPES/STiO₂ (0.5%), (c) SPES/ STiO₂ (1%), (d) SPES/ STiO₂–PANI (0.5%) and (e) SPES/ STiO₂–PANI (1%).

Fig. 8. DSC thermogram of pristine SPES and SPES composite membranes.

Fig. 1. Schematic representation of Polyaniline coated sulfonated TiO_2 nanoparticles

Fig. 2. ^1H -NMR spectra of PES and SPES.

Fig. 3. FTIR spectra of TiO₂, STiO₂ and STiO₂-PANI.

Fig. 4. FTIR spectra of pristine SPES and SPES composite membranes.

Fig. 5. XRD pattern of STiO₂ and STiO₂-PANI.

Fig. 6. XRD pattern of pristine SPES and SPES composite membranes.

Fig. 7. FESEM images of the membranes (a) SPES, (b) SPES/STiO₂ (0.5%), (c) SPES/STiO₂ (1%), (d) SPES/STiO₂-PANI (0.5%), and (e) SPES/STiO₂-PANI (1%).

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