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## Controlled sulfonation of poly(ether sulfone) using phthalic anhydride as catalyst and its membrane performance for fuel cell application

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**Abstract:** Proton exchange membrane (PEM) fuel cells are one of the most emerging alternative energy technologies under development. A novel proton exchange membrane sulfonated polyethersulfone (SPES) was developed by homogeneous method using phthalic anhydride as catalyst and chlorosulfonic acid as sulfonating agent to control the sulfonation reaction. The method of sulfonation was optimized by varying the reaction time and concentration of the catalyst. The structure of the SPES was studied by <sup>1</sup>H-Nuclear Magnetic Resonance, Fourier Transform Infra Red Spectroscopy and X-ray diffraction. The extent of sulfonation was determined by ion exchange capacity studies. The thermal and mechanical stabilities were studied using thermogravimetric analysis (TGA) and Dynamic Mechanical Analysis (DMA) respectively. DMA results show that the storage modulus increased with increase in degree of sulfonation (DS) and water uptake of SPES increased with DS. The proton conductivity of SPES (34% DS) measured by impedance spectroscopy was found to be 0.03S/cm at 80%RH and 100°C. Also, current-voltage polarization characteristics of SPES membranes offer a favourable alternative PEM due to the thermal stability and cost effective than perfluorinated ionomers.

**Keywords:** PEM; Sulfonated poly (ether sulfone); Phthalic anhydride; <sup>1</sup>H-NMR; DMA

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**1 Introduction:** In recent years, fuel cell is emerging as a most promising alternative clean and renewable energy technologies for generating power for automobile and portable devices [1-2]. Nafion® (DuPont) is the only efficient membrane commercially available for fuel cell application since it has high proton conductivity, chemical and mechanical stability [3]. Uses of Nafion membranes are limited due to loss of conductivity at high temperature, low water retention, high cost of manufacture and environmental problem of synthesis and disposal due to fluorine content. These limitations of present perfluorinated PEM have stimulated the development of less expensive and more environmentally friendly PEM materials like Poly(benzimidazole), Poly(sulfones), Poly(ether ketones) etc [4-9]. Poly(ether sulfone) (PES) is one of the high performance engineering thermoplastic materials having excellent thermal and mechanical properties as well as high resistance to oxidation and acid catalyzed hydrolysis [10]. Sulfonation of PES improves their expected membrane properties such as hydrophilicity, higher water flux, permeability and proton conductivity [11-13]. Therefore, sulfonated poly(ether sulfone) (SPES) is considered as an attractive material for PEM fuel cell [14-16].

Various methods of sulfonation have been tried to introduce the pendant sulfonic acid groups into the PES [17-23]. In this research work, emphasis has been given on controlled sulfonation reaction using chlorosulfonic acid as sulfonating agent and phthalic anhydride as catalyst. Till now no research work has been reported using phthalic anhydride as catalyst for activating the chlorosulfonic acid. Phthalic anhydride has maximum tendency to attach sulfonic acid group stereospecific at ortho position of the

aromatic backbone of PES. The reaction has been carried out at low temperature to avert low molecular weight products and side reactions. The possible reaction mechanism is shown in given below figure 1. A series of sulfonated Poly (ether sulfone) (SPES) samples with different DS were prepared. The spectroscopic studies of SPES have been carried out by FTIR, and NMR. The structural determination of SPES has been done by X-ray diffraction analysis. The thermal stability of SPES has been measured by thermogravimetric analysis and the mechanical properties were measured by dynamic mechanical analyser. The proton conductivity has been measured by impedance spectroscopy and its performance analysis was studied by H-Tec Fuel cell set up.

## 2. Experimental

**2.1 Materials:** PES (RADEL A-300) was purchased from Solvay Advanced Polymers. Chlorosulfonic acid was purchased from Loba Chemie. Concentrated sulfuric acid and N-methyl-2-pyrrolidone (NMP) were purchased from Aldrich chemicals. 1, 2-Dichloromethane and phthalic anhydride were obtained from S d fine Chemicals.

**2.2 Sulfonation:** Sulfonated polyether sulfones of different degree of sulfonation were prepared by the following procedure. Initially 100ml of concentrated (95-97% strength) sulfuric acid was mixed with 35 ml of chlorosulfonic acid in a conical flask.

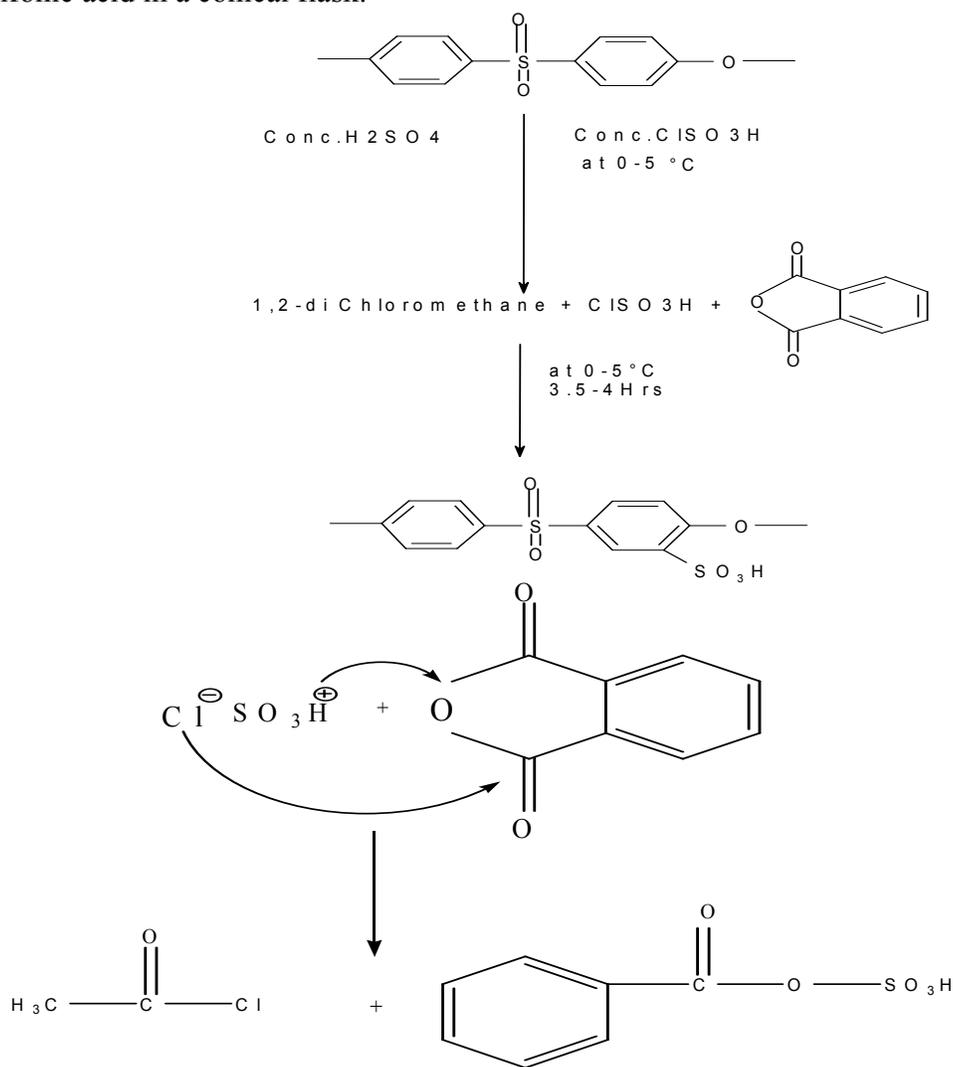


Figure 1: Reaction mechanism for activating the sulfonating agent, - Chlorosulfonic acid.

The temperature of the acid mixture was maintained at 0 °C in a cryobath. Then 20 gm of PES, pre-dried in a vacuum oven at 110 °C for 10 hours, was dissolved in this solvent mixture to form a homogenous solution. After attaining a homogeneous mixture, 50 ml of dichloromethane was added to it. The solution was then cooled to 0 °C, under continuous stirring condition. Within 30 minutes, 4 ml of chlorosulfonic acid was added dropwise to the polymer solution and 8ml of phthalic anhydride (catalyst) was then added to initiate the catalysed sulfonation reaction. The reaction time was varied to obtain samples of different degree of sulfonation. The mixture was precipitated into ice-cold deionized water and the resulting precipitate was filtered and washed with deionized water until pH was 6~7. The reaction time was optimized to 4.5 hrs at 5±2 °C to achieve desired degree of sulfonation (DS).

**2.3 Membrane Preparation:** The membranes were prepared by dissolving SPES in NMP solvent to form a 20 wt% solution, and then cast on a clean glass plate using membrane-casting apparatus. The membranes were dried in an oven programmed at different temperatures to control the solvent evaporation rate. Final drying was done by placing the membrane in a vacuum oven at 100°C for more than 2 days, to remove the solvent. The membranes having thickness 20±5 µm were obtained by varying the distance between the knife and the glass plate during the casting process. The sample codes of the membranes with different degree of sulfonation are given in Table 1.

Table1. Sample Code:

Sample Name	Time of reaction (Hrs)	Degree of Sulfonation (DS)
SPES1	3hrs 45min	5.2
SPES2	4hrs	11.8
SPES3	4hrs 15min	20
SPE4	4hrs 30min	34

### 3. Results and Discussion:

**3.1 Spectral Characterizations:** The sulfonation site of PES and SPESs were determined by <sup>1</sup>H NMR spectroscopy (Bruker Advance-400). As shown in Fig. 2, the presence of a sulfonic acid group causes a significant down-field shift from 7.3 to 8.3 ppm of the hydrogen located in the σ-position at the aromatic

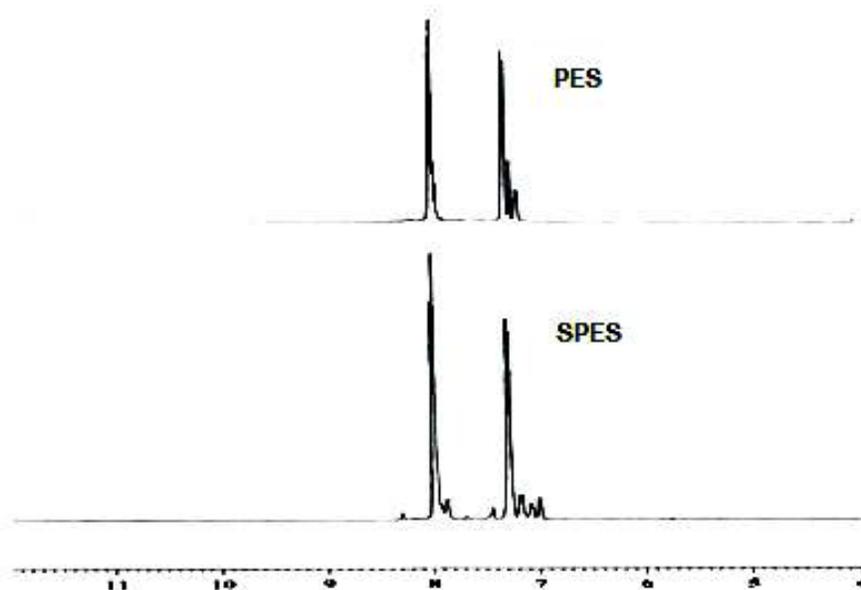


Figure 2: The <sup>1</sup>H NMR spectrum of PES and SPES.

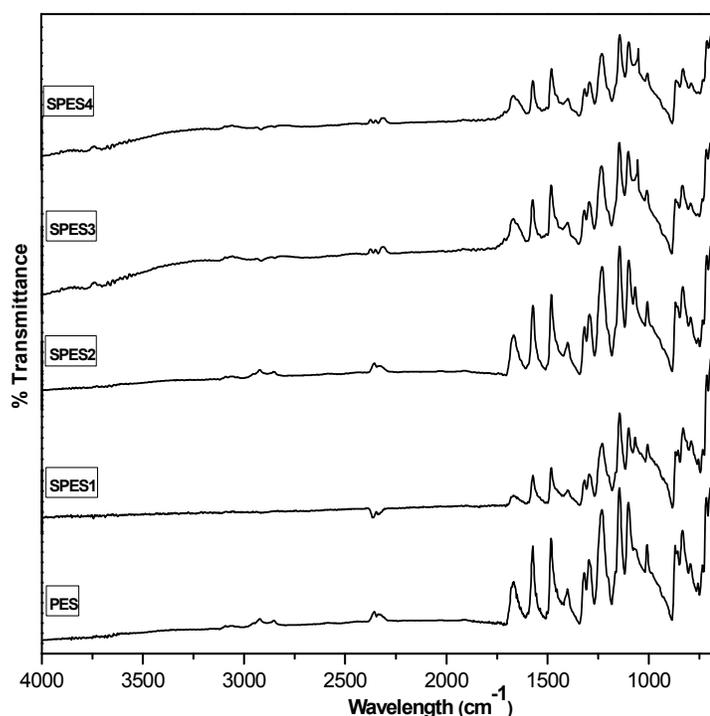


Figure 3: FTIR spectra of PES and SPES.

ring [22]. This downfield shift is attributed to the attachment of the electron-withdrawing sulfonic acid group to the aromatic carbon.

The introduction of the sulfonic acid groups was also confirmed by the IR- Prestige 21 FTIR spectrometer (Shimadzu Corporation, Japan) (Figure 3). The major difference in spectra of PES and SPES is the presence of an absorbance at about  $1153\text{ cm}^{-1}$  in the SPES, which is attributed to the asymmetrical stretching of the sulfonic acid groups [11]. The symmetrical stretching vibration of

Table2: FTIR wavenumber and absorbance value at  $1153$  and  $1263\text{ cm}^{-1}$ .

Sample	Wavenumber at $\sim 1153\text{ cm}^{-1}$	$A_{1153}$	$A_{1263}$	$A_{1153}/A_{1263}$
SPES1	1150.7	0.786	0.995	0.79
SPES2	1151.50	0.796	0.993	0.80
SPES3	1153.2	0.883	0.966	0.91
SPES4	1154.2	0.892	0.945	0.94

sulfonic acid group is at  $1025\text{ cm}^{-1}$ . The regular changes in the characteristic absorption peak at  $\sim 1153\text{ cm}^{-1}$  compared with an internal standard, absorption peak at  $\sim 1263\text{ cm}^{-1}$  attributed to sulfone group, as shown in Table2, where  $A_{1153}$  and  $A_{1263}$  are the absorbance values at  $\sim 1153$  and  $\sim 1263\text{ cm}^{-1}$  respectively [8]. Another evidence of the presence of sulfonic acid group is the appearance of the peak at  $3460\text{ cm}^{-1}$  in SPES samples, which is assigned to O-H vibration from sulfonic acid group. This has been also reported by Guan et al. [22].

**3.2 Determination of Ion Exchange Capacity (IEC) and water uptake of SPES:** The ion exchange capacity (IEC) and degree of sulfonation (DS) were determined by titration and calculated using following equation [18].

$$DS(\%) = \frac{0.232M(\text{NaOH}) \times V(\text{NaOH})}{[W - 0.08(\text{NaOH}) \times V(\text{NaOH})]} \times 100 \quad (1)$$

$$IEC = \frac{1000DS}{(232 + 81 \times DS)} \quad (2)$$

where  $M(\text{NaOH})$  is the concentration of standard NaOH solution (mol/l),  $V(\text{NaOH})$  the NaOH solution volume used to neutralize (ml),  $W$  the sample mass (g), 232 the molecular weight of PES repeat unit and 81 the molecular weight of the sulfonic acid group ( $-\text{SO}_3\text{H}$ ).

Table3. DS and IEC of SPES samples

Polymer	SPES-1	SPES-2	SPES-3	SPES-4
DS from titration (%)	5.2	11.8	20	34
IEC (meq/gm)	0.22	0.49	0.80	1.31
Water Uptake at 25°C (%)	7.09	10.33	14.66	19.05

The SPES membranes show increased IEC and water uptake with increased DS as shown in table 3 which may be due to strong hydrophilicity of the sulfonic acid groups. A relation between

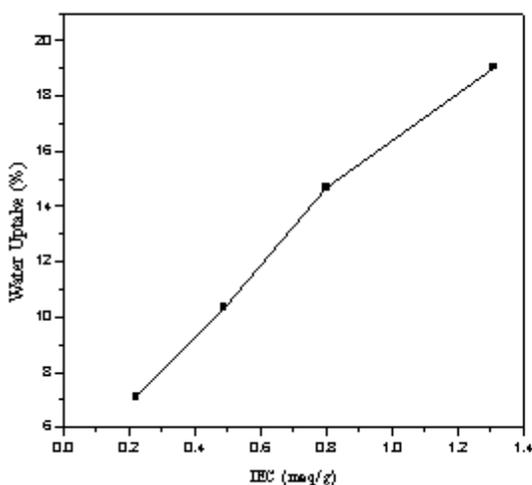


Figure 4: Water uptake as a function of IEC for SPES of PES membrane at 25°C.

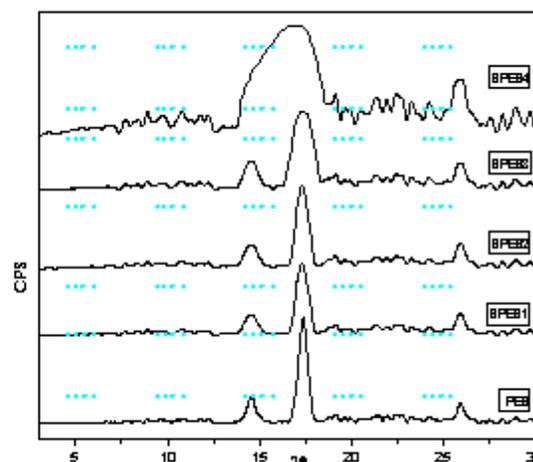


Figure 5: X-ray diffraction analysis diagram and SPES.

the IEC and water uptake of membranes is illustrated in Figure 4. In proton exchange membranes, the proton conductivity depends on the number of available sulfonic acid groups and their dissociation capability in water. The absorbed water in PEM promoted the phase separation which results in membrane collapse and dimensional change leading to failures in mechanical properties and in extreme cases, solubility in water at elevated temperature.

**3.3 XRD:** Diffraction patterns of the PES and SPES membranes were obtained on a Rigaku Miniflex X-ray Diffractometer (Japan) are shown in Figure.5. The patterns for all membranes showed broad peaks at  $2\theta = 17.3^\circ$  ( $d = 5.12 \text{ \AA}$ ). However, with the increase in degree of sulfonation, the pattern of SPES membrane shows a broadened peak with reducing peak intensity. The reduced peak intensity may be due to less order of macromolecular orientation within the polymer [4, 8].

**3.4 Thermal and Mechanical Properties:** The thermo gravimetric analysis (TGA) (DTG-60, Shimadzu, Japan) for PES and SPES in Figure 6 gives the three transition regions of weight loss in three different temperature ranges. The first transition in weight loss is around 100°C due to the loss of the absorbed water molecules. The second weight loss region, observed between 200°C to 300°C, can be attributed to the decomposition of the sulfonic acid groups. The third thermal degradation region of SPES at about 600°C is assigned to the degradation of the polymer main chain. The sulfonated samples show lower decomposition temperatures may be due to the

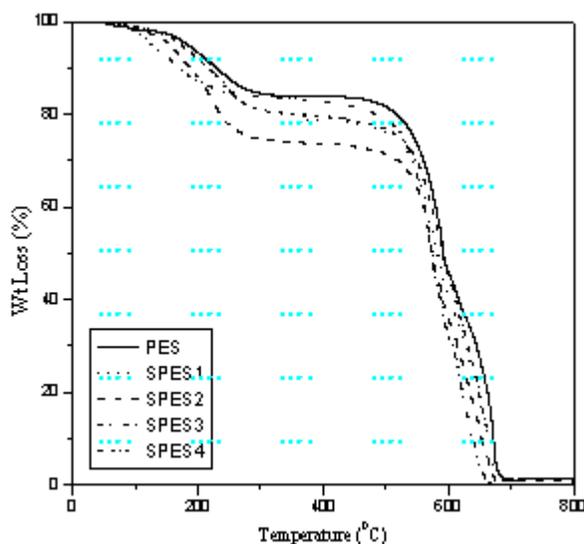


Figure 6: TGA traces of PES and SPES.

introduction of sulfonic acid groups that renders it irregular and less stable and finally, enhanced asymmetry structure of PES. Nafion 117, which showed 25% weight loss at 250°C whereas SPES have only 15% wt loss at the same temperature [8, 11, 24].

The thermo-mechanical properties of the synthesized sulfonated PES films were measured using DMA (Dynamic Mechanical Analyzer, Q 800 TA instruments). The variations in the tensile storage modulus ( $E'$ ) with different DS in PES as a function of temperature are shown in Figure 7a. The storage modulus for the neat PES membrane is observed to be  $5.8 \times 10^3$  Pa and for all the sulfonated PES membranes the values are around  $6.2 \times 10^3$  Pa. With gradual increase of DS, the  $E'$  value also increased due to introduction of polar group i.e, sulfonic acid groups in the backbone aromatic ring of PES, which allows stress transfer from PES backbone to sulfonic acid groups. Figure 7b shows the tan delta ( $\tan\delta$ ) value reduced as the introduction of sulfonic acid groups on the aromatic ring of the backbone of PES increases. The glass transition temperature ( $T_g$ ) of the membranes determined from the  $\tan\delta$  peak is 235°C for neat PES and 238°C, 239°C, 241°C and 243°C for polymer membranes SPES1, SPES2, SPES3 and SPES4 respectively. There increase in  $T_g$  as DS increases in comparison with the virgin polymer is due to increased sterical hinderance when a hydrogen atom in an aromatic ring is replaced by a sulfonic acid group [25].

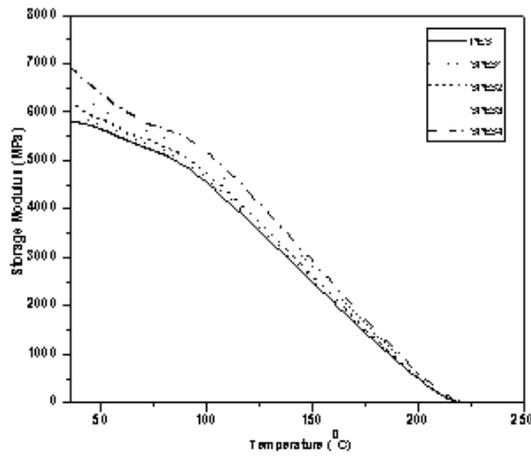


Fig.7a: Storage modulus of SPES as a function of temperature.

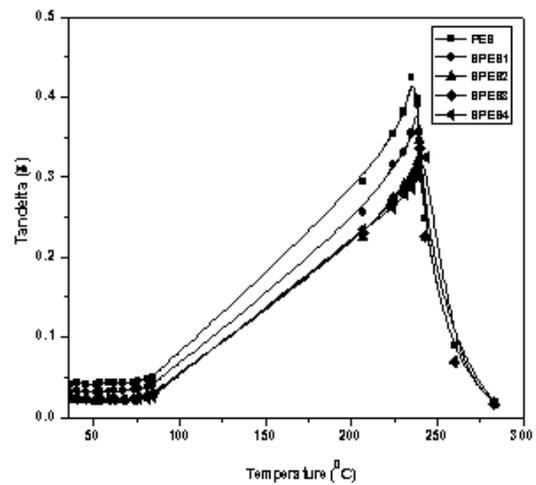


Fig.7b: Tanδ of SPES as a function of temperature.

**3.4 Proton Conductivity:** A typical complex plane plot of real impedance ( $Z'$ ) vs imaginary impedance ( $-Z''$ ) for SPES membranes measured by using an AC impedance spectroscopy of Novocontrol Technologies in the frequency range 1Hz–10MHz hydrated in 80% relative humidity (RH) environment is shown in Figure 8. The conductivity,  $\sigma$ , of the samples in the transverse direction was calculated from the impedance data, using the relation

$$\sigma = (RA/d)^{-1} \tag{4}$$

where R is the membrane resistance( $\Omega$ ), derived from the high frequency intercept with the real axis on a complex impedance plane plot, A is the cross sectional area of the membrane ( $\text{cm}^2$ ), and the d is the distance between the electrodes(cm).

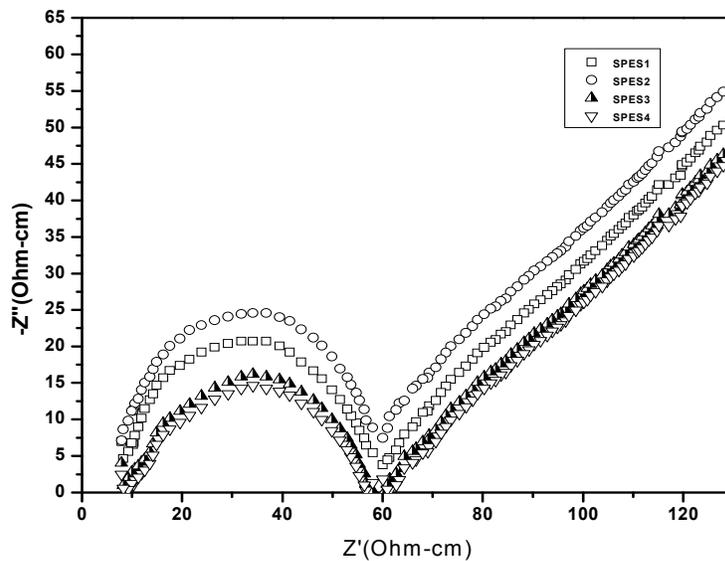


Figure 8: Complex-plane impedance plot for SPES with different DS in 80%RH at 80°C.

The conductivity increased linearly with increasing DS and the conductivity of PES with DS 34% measured as 0.03S/cm at 80% RH using impedance spectroscopy that is comparable to conductivity of Nafion (0.08S/cm) [26]. It is observed from the data shown in Table 4 that the

Table 4: Ionic conductivity of sulfonated polymer and Nafion 117

Temperature (°C)	DS	<u>Proton Conductivity (mS/cm)</u>			
		40	60	80	100
Membrane	DS				
SPES1	5.2	0.4634	0.4654	0.4657	0.4684
SPES2	11.8	0.8894	0.90991	0.9131	0.9198
SPES3	20	0.9539	0.9613	0.9616	0.9667
SPES4	34	2.7363	2.7461	2.7569	2.7685

conductivity of SPES membranes increased with increasing degree of sulfonation. It has been suggested that the migration of proton through the membrane became easier with increasing in number of sulfonic acid groups. The conductivity is also increases with increase in temperature. When the degree of sulfonation increased to a sufficient level (i.e. DS of 34%), the ionic domains become more interconnected and simultaneously overcome the diffusion limitations and allow the ionic conductivity to reach a maximum value [27, 28]. The proton conduction in these polymers is based on the migration of hydronium ions  $[(H_2O)_nH^+]$  through the hydrophilic clusters of sulfonic acid groups [29, 30].

**3.5 Current-voltage polarization studies in H<sub>2</sub> fuel cell:** The current-voltage polarization curves were recorded with the help of H-Tec fuel cell set up with controlled gas flow, pressure and temperature regulation attached with electronic load control using H-Tec fuel cell monitor 2.0 software. The membranes (SPES1, SPES2, SPES3 and SPES4) used for current–voltage polarization curves had planner area of 25 cm<sup>2</sup> (5cm×5cm), and was pressed between the electrodes of PEMFC Kit 1919.

The single-cell performance curves plotted in figure 9 show that SPES membranes perform practically well in an MEA for DS>20%. The results were consistent with the probable increase in performance of the membrane in the MEA with increasing IEC as shown in figure 4. As evident from figure 8, SPES4 membrane performance was superior primarily in the low current density region. Also SPES4 showed relatively higher power density at a given current density than other SPES membranes.

These may be attributed to specific membrane conductivities of these membranes [31]. Furthermore at given voltage at given current density dependent on membrane-electrode delamination in the membrane electrode assembly. Moreover, the voltage at given current density for SPES membranes suggest the suitability of Hydrogen PEMFC applicability.

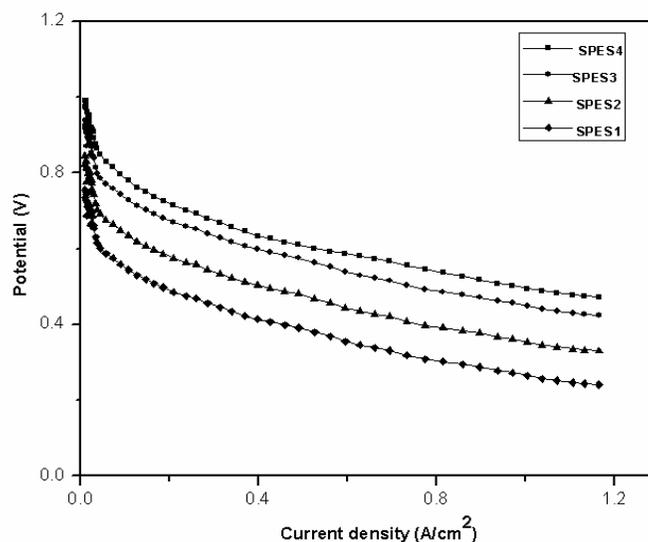


Fig. 9: Effect of sulfonation level on single cell potential vs. current density plots for SPES at 25°C, 1atm and 75% RH and using H<sub>2</sub>/O<sub>2</sub>.

**4. Conclusions:** The more economic and effective controlled sulfonation of PES was achieved using chlorosulfonic acid as sulfonating agent and phthalic anhydride as catalyst along with varying the reaction time at lower reaction temperature. The sulfonic acid group introduced at ortho position of PES was confirmed by <sup>1</sup>H NMR and FTIR. X-ray diffraction patterns confirmed the crystallinity of SPES membranes decreases with increase in degree of sulfonation. IEC and water uptake shows that proton conductivity depends on the number of sulfonic acid groups and their dissociation capability in water. It has been evident from the TGA that the degradation temperature and glass transition temperature of the PEM were above the normal operating temperature (100°C) of fuel cell which assure that it has better thermal stability than commercially used Nafion 117. Its mechanical properties retain upto 200°C which have been supported by DMA. The proton conductivity increases with increasing temperature and comparable with Nafion membrane at 80°C. The current-voltage polarization characteristic of synthesized SPES membrane renders them applicable to H<sub>2</sub> fuel cell. The development of PEM via eco-friendly route may provide inexpensive and easy synthesis process for controlled sulfonation of PES. However, the high T<sub>g</sub> of the SPES together with its hydrophilic nature and good proton conductivity, suggested that this polymeric membrane may be useful as promising proton exchange membrane for fuel cell at high temperature operation.

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