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INEXPENSIVE PROTON EXCHANGE MEMBRANE SYNTHESIS BY SULFONATION OF COMMERCIALLY AVAILABLE POLYCARBONATE

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Commercially available thermoplastic, bisphenol polymer (polycarbonate) was sulfonated with various reagents to introduce sulfonic acid group (SO_3H) under optimum conditions. Subsequently modified polymer was studied for its physical and chemical properties needed for its potential use as PEM in Fuel Cells (FCs). Fourier Transform Infrared (FT-IR) and X-ray Diffraction (XRD) were performed to confirm the occurrence of sulfonation. Differential Thermal Analysis (DTA) and Themogravimetric Analysis (TGA) were used to determine the effects of sulfonation on glass transition temperature (Tg) and thermal stability of modified polymer. The Ion Exchange Capacity (IEC) and Degree of Substitution (DS) of sulfonic acid group were determined using standard procedure. Swelling properties were tested using water soaking. Scanning Electron Microscopy (SEM) was utilized to study the morphology of the polymeric membrane both before and after sulfonation. The results reveal that proper controlled sulfonation of bisphenol polymer can be a viable substitute for NAFION owing to its comparable IEC (1.15 meq/g), DS, water uptake (35%), good mechanical properties/ thermal stability and above all low cost of production.

Keywords: Proton exchange membrane (PEM), Fuel cell (FC), Bisphenol polymer, Sulfonated polycarbonate (SPC)

1. Introduction

Recently, Fuel Cell is considered one of the promising future alternate energy generation chemical device for automobile, stationary applications and portable equipments. PEMFC system has numerous advantages such as high power density, quick start up, low temperature operation and rapid response to loads [1-2]. One of the most challenging problems, which is retarding its common use is the cost of the PEM. Its expense can be tolerated in special cases, as in the case of the Gemini space programme in 1965 [3] but to make it popular and economical in relation to other existing technologies, cost has to be brought down by development of new inexpensive PEM polymers.

At the moment Nafion a product of Dupont [4], perfluorosulfonic acid polymers is the most widely used PEM in the fuel cells. It possesses high ionic conductivity, good thermal stability, high mechanical strength and excellent chemical resistant. However, high cost ($800/m^2 correspond to $160/ KW) [5], structural instability at >100°C and low conductivity at low relative humidity [6] has instigated search for cheaper versions. Therefore, many polymers have been investigated to assess their feasibility as PEM candidates e.g. Polystyrene, [7], Poly (arylene–ether–sulfone) (PES) [8-11], polyether ether ketone (PEEK) [12-15], Teflon-FEP graft Styrene [16], styrene grafted polytetrafluroethylene (PTFE) [17], PVDF-graft styrene [18,19], Chitosan- olyacrylic acid complex [20] acid doped Polybenzimidazole (PBI) [21], Polyphosphazene [22,23], Poly (phenylquinoxalines) (PPQ) [24], and Poly (Phenylene Oxide) (PPO) [7]. Required properties of a PEM for FC to make it compatible to other technologies are low-cost (less than $10/kW, high proton conductivity, good chemical stability and mechanical integrity in hot water. Todate none of the proposed materials satisfy the desired specification. Common problems come across in most studies were low proton conductivity at low sulfonating agent concentration. It has been observed in previous studies that when the polymers were treated with concentrated sulfonating agent, the proton conductivity increases but at same time it causes swelling, significant decrease in strength and also produces solubility of polymer in water. Inspite of

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this Sulfonation in certain precise conditions is considered a powerful and versatile process. It can be used to simultaneously render polymers proton conductivity as well as hydrophilic nature. Certain polymers can be sulfonated in the initial stages of synthesis or can be sulfonated in their final form depending on there applications.

In this article, preparation of PEM by sulfonation of a polycarbonate (PC) is reported. After sulfonation polymer membranes were characterized and investigated for their properties. This involved measurement of IEC, DS, water uptake or hydrophilicity, the membrane resistance to high temperature and surface morphology to support transfer of proton from one side to other.

2. Experimental

2.1. Materials

Sulfuric acid, Chloroform: (>99.5% pure), Methyl alcohol: (99.8% pure, HPLC- grade), were purchased from BDH chemicals Ltd. Poole, England. Sodium hydroxide was obtained from Aldrich Chemical. Chlorosulfonic acid used was purchased from Merck (E.Merck, Germany). All chemicals were used as received without any further purification. Polycarbonate was purchased from General Electric Plastics, USA and was used as such.

2.2. Sulfonation

2.2.1. Choice of sulfonating agent

Two different reagents, sulfuric acid, and chlorosulfonic acid were used to sulfonate the PC film. Methanol was used to wash the PC film which was dried in an oven at 50°C for 24 hours before sulfonation. The criteria for selection of the best reagent were based on its ability to sulfonate PC and to enhance its ion exchange capacity (IEC) without appreciably decreasing its mechanical strength at 80 °C, the common working temperature of a fuel cell.

Sulfuric acid:

Sulfonation was performed with concentrated sulfuric acid (98%) for different intervals of time using pre prepared PC film. For this purpose 0.5g of PC sheets were immersed in concentrated sulfuric acid. The samples were kept over-night at room temperature for sulfonation. Polymer films were washed carefully with de-ionized water to remove the excess acid on the surface. After washing, the samples were dried first at room temperature for a day then at 50°C for another day and subsequently kept in a desiccator to remove the remaining moisture until the samples attained constant weight.

Chlorosulfonic acid:

PC was also sulfonated using chlorosulfonic acid. Due to the hygroscopic nature of chlorosulfonic acid it was diluted in chloroform [25]. The reaction was carried out in a Petri dish to prepare the sulfonated polycarbonate by simultaneous sulfonation and film forming process. Different molar concentrations of acid (0.056, 0.075, 0.113, 0.15, and 0.225 M) were used for sulfonation. 30% (W/V) of polymer were immersed in each petri dish containing 10ml of the above mentioned acid concentrations. The petri dishes were covered for 3 hours. During the sulfonation reaction the film first dissolves in the sulfonating solution and reforms after evaporation of the chloroform in the sulfonating solution. After 3 hours the Petri dishes were uncovered and the samples were allowed to air dry in a fumehood. After drying of the films they were removed from the petri dishes by immersing them in deionized water to facilitate the removal of the films without any damage. Films were washed with deionized water until there was no acid in the water, which was checked by monitoring the pH of the water. After sulfonation the films were dried at room temperature for 48h, then oven dried at 50˚C for a further 48h. The films were then placed in a desiccator for several days until constant mass was achieved. Optimum sulfonation was achieved by varying acid concentration.

2.3. Change in physical and chemical properties after sulfonation.

Prior to the characterization step, the removal of residual solvent and any moisture from the samples is of prime importance as the residue solvent has dramatic effect on membrane properties. For this purpose samples were dried in an oven at 80˚C for 72 hours then kept in a desicator for a further 24 hours.

2.3.1. Change in mass and thickness of PC film/ membrane.

The mass of the membranes was measured using an electronic balance (Sartorius Digital, BP 221S, Max. = 220g, Min. = 0.0001). Membrane thickness was measured using a digital length gauge, (HEIDENHAIN METRO, MT 12, Max.= 10mm, Min. =1µm, Accuracy = ±1µm) after sulfonation. Results are shown in Figure 1.

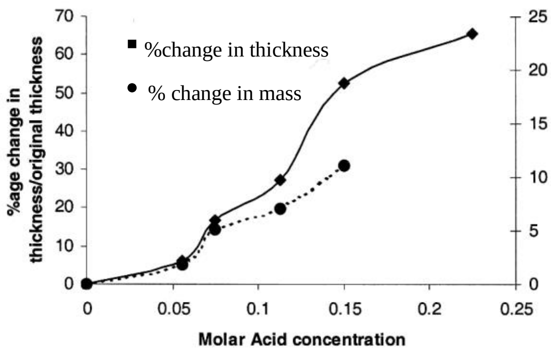


Figure 1. Percentage change in thickness and mass of film with variation of acid concentration.

2.3.2. *Determination of ion exchange capacity (IEC)*

Ion-exchange capacity (IEC) was determined by an exchange of acidic protons with Na^+ ions in solution [26, 27]. The membranes were dried and weighed and then placed in 35ml of 3M NaCl solution at room temperature overnight and then at 50°C for 3 hours to exchange Na^+ ions with H^+. A large excess of Na^+ ions in the solution ensured nearly complete ion exchange. The membranes were removed from the solution and the solution was titerated against 0.05M NaOH solution using phenolphthalein indicator to determine the end point and the quantity of exchanged H^+ ions. The IEC was calculated using the dry weight of the polymer.

$$\text{IEC} = \text{M} \cdot \text{V} \cdot \frac{3.5}{\text{m}} \qquad (1)$$

Where IEC is the ion exchange capacity (meq./g), M is molarity of NaOH used, V is the volume of NaOH used for titration, 3.5 is the factor corresponding to the ratio of the amount of NaCl taken to immerse the polymer to the amount used for titration, and m is the mass of sulfonated sample in grams(g).

2.3.3 *Degree of substitution (DS)*

The degree of substitution (DS) indicates the average number of sulfonic groups present in the sulfonated polymer. Relationship between DS and IEC [7] is

$$\text{DS} = \frac{120 \cdot \text{IEC}}{1000 + 120 \cdot \text{IEC} - 200 \cdot \text{IEC}} \qquad (2)$$

The IEC & DS results obtained in this study are given in Figure 2.

2.3.4 *Water uptake*

In order to determine the water uptake, weighed dried circular pieces of 5 cm diameter sulfonated and non-sulfonated PC membranes were immersed in liquid water under atmospheric pressure at ambient temperature. The membranes were removed from the water sorption vessel and surface water brushed off to get accurate membrane water content at the particular time t. The film was then quickly re-immersed in the water. The process was repeated until the film attained steady state as indicated by the film's constant weight. The degree of swelling or water uptake was calculated from:

$$\text{Percentage Water Uptake} = \frac{(M_s - M_d) \cdot 100}{M_d} \qquad (3)$$

Where M_s and M_d are the masses of the swollen and dry polymers, respectively, in grams. Figure 3 gives the relationship of IEC to Water uptake with the variation of sulfonating agent concentration.

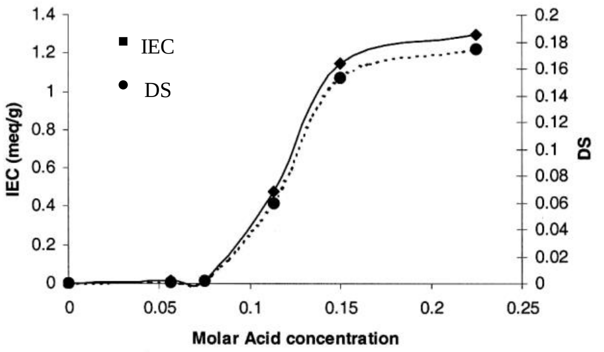


Figure (2) Change in IEC in meq./g and DS with variation of acid concentration.

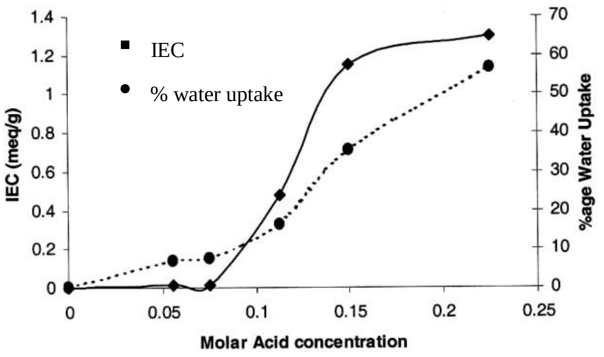


Figure 3. Relationship of IEC and water uptake at different acid concentration.

2.4. *FTIR studies*

The FTIR spectra of non-sulfonated and sulfonated membranes were scanned using FT-IR spectrometer (MIDAC Corporation, M-Series, and Irvine, California, USA). FTIR spectroscopy does not require a vacuum, since neither oxygen nor nitrogen absorbs infrared rays. FTIR analyses can also be applied to minute quantities of polymeric material. Spectra are shown in Figures 4 and 5.

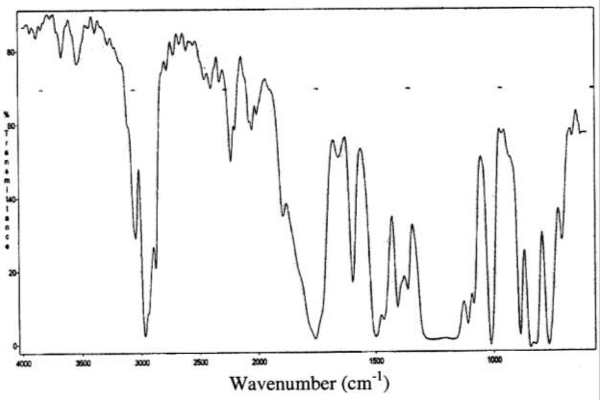


Figure 4, FT-IR Spectrum of Polycarbonate.

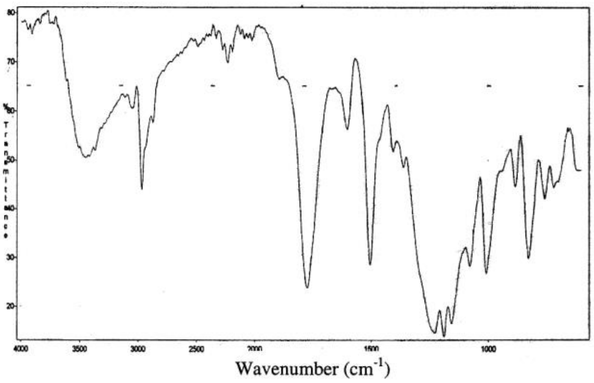


Figure 5. FT-IR spectrum of sulfonated polycarbonate.

2.5 *X-ray diffraction*

The X-ray diffraction spectra of PC and SPC were obtained from the polymeric films using a “Panalytical X’ Pert PRO”, Multipurpose Diffractometer (MPD) in a continuous scan with a step size of 2θ equal to 0.04° and scan speed of 0.1333° S^{-1}, ranging between 2θ equal to 0° and 90°. Voltage and current used for analysis were 40 KV and 40 mA respectively. The selected portions of the spectra obtained are shown in Figure 6.

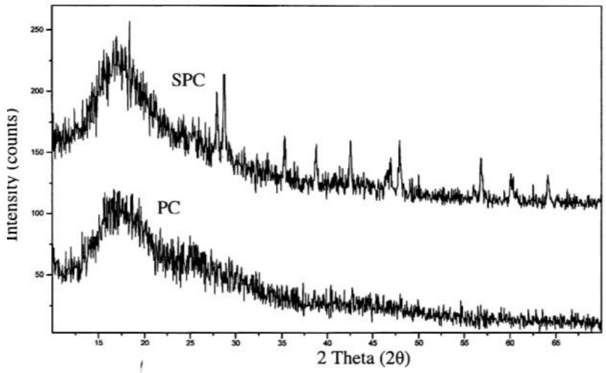


Figure 6. XRD spectra of Polycarbonate (PC) and Sulfonated Polycarbonate (SPC).

2.6 *Thermal analysis*

Thermal analysis, differential thermal analysis (DTA) and themogravimetric analysis (TGA), of PC and SPC samples was carried out on a Simultaneous Thermal Analyzer (Netzsch STA 409). Pre-weight samples of PC and SPC were analyzed separately in alumina crucibles. DTA/TG analysis was performed under air and nitrogen atmosphere separately. The temperature range used was room temperature to 800 °C for air and room temperature to 950°C for nitrogen atmosphere with increase rate of 10°C /min. The reference material used for DTA was alumina Al_2O_3, which is an inert material. Air was used to remove volatiles emitted from the analyte. Thermogram of PC and SPC are shown in Figures 7 and 8.

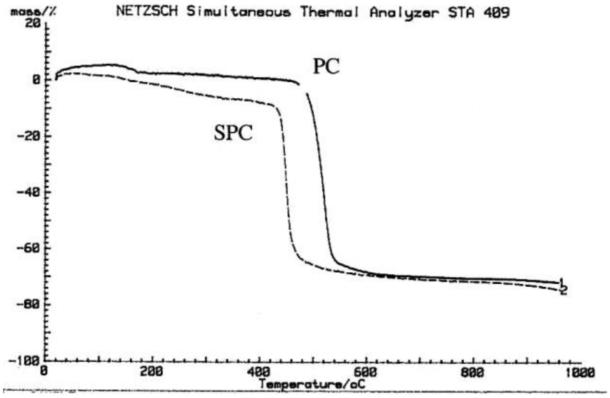


Figure 7. TG curves of Polycarbonate (PC).and Sulfonated polycarbonate analysed in N_2 atmosphere.

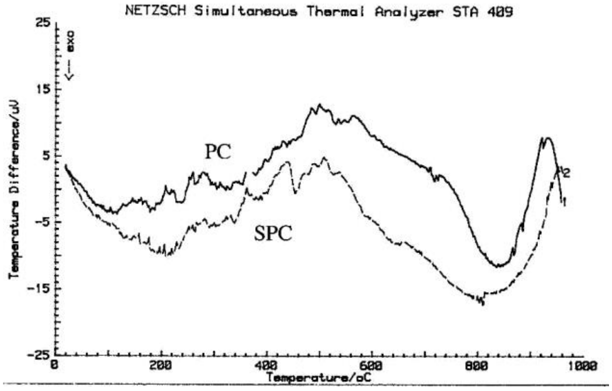


Figure 8. DTA curves of Polycarbonate (PC).and Sulfonated polycarbonate (SPC) analysed in N_2 atmosphere

2.7 *Scanning electron microscope (SEM) studies*

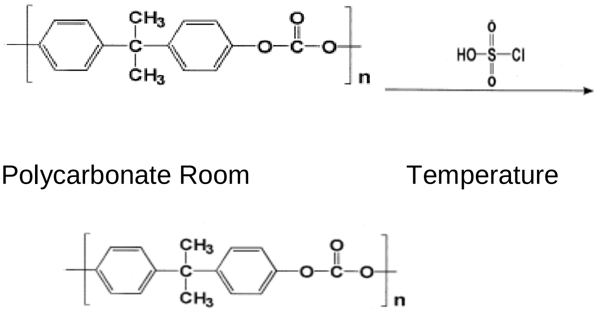
Scanning electron microscope, (SEM, LEO 440, UK, Magnification = 5X – 300,000X, Resolution = 3.5 nm) was used for the morphological analysis of the sulfonated and non- sulfonated samples. For SEM analysis, small pieces of PC and SPC samples were pasted onto aluminum stubs with silver paste. Once the paste was dry the films were coated with a thin layer of gold (Au) by sputtering technique using a Magnetron sputtering device (MSD). The gold-coated samples were placed in the SEM sample chamber and analyzed at different magnification (100, 500, and 1000X). The detector used was a secondary electron (SE) detector. SEM images are shown in Figure 9.

3. Results and Discussion

The present research focused on the development of proton exchange membranes for fuel cell application. Therefore experiments were conducted to sulfonate and characterize polycarbonate membranes. A variety of chemical and physical, properties, which are thought to be important parameters for fuel cell performance, were investigated and are discussed below.

3.1. *Sulfonation of polycarbonate (PC)*

The ion exchange capacity (IEC) and degree of substitution (DS) of PC films sulfonated with H_2SO_4 revealed that sulfonation did not occur even when concentrated sulfuric acid was used. Hence sulfuric acid was considered unsuitable for the sulfonation of PC. Chlorosulfonic acid was used as a sulfonating agent according to the procedure mentioned previously in section 2.2. PC membranes were found to undergo sulfonation with chlorosulfonic acid via the reaction:



Polycarbonate Room Temperature

(4)
Sulfonated polycarbonate

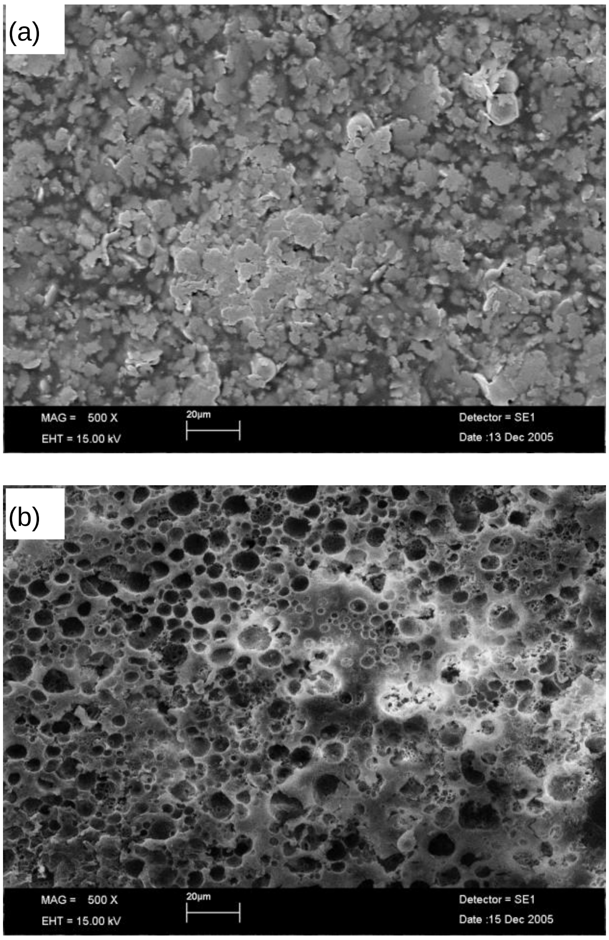


Figure (9) SEM Micrographs of (a) PC And (b) SPC at 500 Times Magnification

3.2. *Change in mass and thickness of PC film/ membrane*

The data presented in Figure 1 shows that the mass and thickness of the resultant product increases with increase in the concentration of chlorosulfonic acid used for sulfonation. More appreciable change is observed in mass and thickness at 1% acid concentration as compared to lower chlorosulfonic acid concentrations. There are two causes due to which this increase in mass and thickness take place; 1) effect of the trapped solvent used for the membrane formation, which is apparent from the results of blank polycarbonate samples 2) effect of chlorosulfonic acid which is highly hygroscopic in nature and causes swelling effect due to absorbed moisture from the atmosphere.

Thickness of Nafion-115 is reported to be 130μm in literature [28], while the data in Table 2 shows that the thickness of the selected SPC of initial mass 0.3g is 126μm, which is close to that of Nafion 115. Thickness is an important factor in proton conduction through polymer membranes due to the fact that if the thickness is less, then the membrane will be more efficient as protons will have a short path to travel. However very thin membranes may not be strong and may not possess the required physicochemical stability. Therefore a compromise is required in which the thickness of the membrane is such that it is strong but also efficient as a proton conductor.

3.3. Ion exchange capacity (IEC) and degree of substitution (DS) of SPC

The ion exchange capacity (IEC) is the principal property, which determines the efficiency of a membrane as a PEM [17]. The values of IEC at different chlorosulfonic acid concentration and using variable initial masses of PC were determined. Their graphical representation shown in Figure 3 illustrates that IEC and DS increase with an increase in Chlorosulfonic acid concentration at constant initial mass of PC used for sulfonation. At higher concentration of chlorosulfonic acid the membrane strength is adversely affected and the film becomes brittle. On the other hand generally an increase in initial mass of PC decreases the IEC. At 1% chlorosulfonic acid concentration, the film of mass 0.1g was physically damaged and started to dissolve which gave erroneous results for its IEC. The membrane, which initially weighed 0.2 g, sulfonated with 1% chlorosulfonic acid has the maximum IEC, but its strength is less than the 0.3g membranes sample, whose IEC is slightly lower than for the 0.2 g sample but due to its better strength properties it is probably more suitable as a PEM. As DS is directly related to the (IEC) and the values of DS were determined from the values of IEC, they show the same trend as IEC.

3.4. Water uptake/ sorption

Water content is very important in efficient functioning of PEMFCs. It is known that typically proton conductivity decreases as the film becomes dehydrated due to elevated temperature. On the other hand water molecules hydrate the protons produced at the anode producing a hydronium-like species, $H^+(H_2O)_n$. So proper water management is vital for proper operation and performance of PEMFCs. Water uptake for the sulfonated polycarbonate was determined in this work according to equation 3. The equilibrium weight was taken as the weight at which no further change in weight was observed. From Figure 4, it is observed that PC treated with low concentration of chlorosulfonic acid absorbs more water than the untreated polymer. This was due to physical swelling effect of chlorosulfonic acid where sulfonation did not take place. On the other hand there is an appreciable increase in water uptake in the case of SPC due to its polar nature. Another parameter studied was the effect of change in initial mass taken for sulfonation. Figure 4 shows that percentage water uptake decreases with increase in mass of PC. This might be due to the distribution effect of equal amount of acid on larger quantity of polymer, so the swelling effect decreases as IEC decrease with increase in mass.

3.5. Relationship between IEC and equilibrium or maximum water uptake

Relationship between IEC and equilibrium for maximum water uptake has also been studied. Figure 5 indicates that water uptake increases with increase in IEC. Decrease in percentage of water uptake occurs with an increase in mass of the polymer taken initially for sulfonation at a constant volume and concentration of acid. So from the above results it is clear that the increase in the amount of material to be sulfonated with the same amount and concentration of sulfonating agent, decreased the DS, IEC and in turn water uptake as all these parameters are inter-related. Therefore, sulfonation can be controlled by changing the amount of polymer used while keeping the concentration and quantity of sulfonating agent constant. Chris Yang et al., [28], has observed similar behaviour for Nafion 115. They found the liquid water uptake for Nafion 115 at 25°C to be (41%) weight percent and water vapour uptake value at 80°C was reported as (18%) weight percent.

3.6. Membrane characterization

Sulfonated PC Membrane prepared by using 0.3g mass, sulfonated with 1.0% acid, having IEC 1.15 meq/g was selected for further characterization. FTIR spectroscopy and XRD were employed to provide compositional characterizations of the blank and sulfonated PC. Themogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were used to explore the thermal behavior of the polymers sulfonated in this investigation. The morphology of the polymer membranes was studied using Scanning Electron Microscopy (SEM). The results and observations made using the mentioned techniques are elaborated in the following sections.

3.6.1. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy is a powerful tool used to characterize and identify functional groups in a material. FTIR has been successfully utilized to characterize sulfonated polymers [29]. Sulfonated polycarbonate (SPC) with the best IEC results were characterised by FT-IR Spectroscopy. The FTIR spectra of blank and sulfonated PC are shown in Figures 6 and 7. Comparison of the blank PC and sulfonated PC film FTIR spectra shows some additional peaks in the spectrum of SPC, which aren't observed in the spectrum of blank PC. These include the typical peaks of SO_3H at 1250–1150 and 1060–1030 cm^{-1}. The strong band at frequency, 1250–1150 cm^{-1}, can be ascribed to the stretching vibration of S=O and the absorption band at 1060– 1030 cm^{-1} is associated with its symmetric stretching band. The newly appeared broad absorption bands at 3400 – 3500 cm^{-1} are attributed to the stretching vibration of the hydroxyl –OH group that came from the sulfonic acid group $–SO_3H$, which verified that the sulfonation was successfully performed. The stretching band of C=O is at 1765–1720 cm^{-1} due to the ester group of PC, while the C – O – C absorbance for asymmetric stretching band is at 1290 – 1180 cm^{-1}, and the peak for O – C – O group lies at 645–575 cm^{-1}. The spectra are somewhat complex due to an overlap of the absorption of the sulfonic group and ester group of PC, therefore, Jin Lee et. al. [27], confirmed the occurrence of sulfonation by NMR analysis of samples having the same features in its FTIR spectra as mentioned in this studies.

3.6.2. X-ray diffraction spectra

X-ray diffraction spectra of the polymer membranes made of PC and SPC are presented in Figure 8. Peaks at specified positions in the case of SPC, even with low intensity indicated that the sample converted from more amorphous to more crystalline. The presence of crystalline nature in the polymer membrane is due to the attachment of the sulfonic acid group with the polymer chain at certain position and also due to the formation of ionic cluster in the SPC membrane. Crystallographic parameters obtained from analysis represents that the crystal system under analysis is monoclinic with sides (a = 8.1310, b = 4.773, c = 8.6335) and angles ($\alpha = \gamma = 90^\circ$ and β = 111.0810).

3.6.3. Thermal properties

Polymers thermal transitions are very important properties of the material, as they dictate the possible applications of the polymer. Differential thermal analysis is one of the important characterization technique utilized for determining the glass transition temperature of polymers. TG/DTA curves of PC and SPC are taken in nitrogen atmosphere at room temperature to 950ºC atmosphere and in air at room temperature to 800ºC. The weight loss stages can be attributed to 1) the loss of moisture absorbed and solvent which was retained during film formation, 2) due to the decomposition of sulfonic groups in the case of sulfonated polycarbonate and 3) the splitting of the main chains before the final decomposition of the material. Figures 9 and 10 are the TG/DTA results in nitrogen atmosphere while in air about similar behaviour was observed as given in Table 1. In both atmosphere the weight loss for the PC is about negligible up to about 120ºC while the weight loss attitude of SPC differ from that of PC in the same temperature range that is due to the absorption of moisture during the sulfonation process and also due to the trapped solvent in the sulfonated polymer matrix. At temperature 120ºC the drop of mass observed for the PC as well as for the SPC in both air and nitrogen atmosphere. This weight loses is attributed to the Tg value. So from the curve it is observed that the value of the Tg remains the same after sulfonation and this value is 120ºC as mentioned in Table 1. The next minute weight lose stage was observed at about 250ºC in the case of SPC which is absent in the case of PC, this distinct weight lose stage can be credited to the evolution of SO_2 gas removed from the acidic moiety attached in the case of SPC which is absent in PC. This value for the loss of

Table 1. Variation of properties with acid concentration.

Molar Concentration of Chloro Sulfonic Acid	IEC (meq.g-1)	DS	%age change in Thickness/ original thickness	%age change in mass/ original Mass	%age Water Uptake
0	0	0	0	0	0.5
0.056	0.011	0.0013	6.08	1.87	6.9
0.075	0.014	0.0016	16.59	5.15	7.69
0.133	0.481	0.06	27.29	7.04	16.53
0.150	1.15	0.153	52.53	11.06	35.54
0.225	1.3	0.175	65.58	Portion of Polymer dissolved	57

Table 2. Thermal analysis of PC and SPC.

Sample	Atmosphere	Tg (ºC)	SO_2 evolution temperature(ºC)	Main chain decomposition temperature(ºC)	Final decomposition temperature(ºC)	Total weight lose (%age)
PC	Air	~120	-	~460	~580	98.90
	Nitrogen	~120	-	~480	-	81.52
SPC	Air	~120	~250	~400	~520	99.18
	Nitrogen	~120	~250	~420	-	82.38

sulfur dioxide group is close to the value mentioned by S. R. Samms [30] for the same group. The very important and main weight lose stage due to main chain degradation occurred at 480ºC for PC and at 420ºC for SPC under N_2 atmosphere and the same degradation was observed at 460ºC for PC and at 400ºC for SPC in air. In the nitrogen atmosphere sharp drop of mass was observed which may be due to the minimal effect of environment to the sample. The comparison of PC and SPC for their main chain decomposition temperature indicated significant decrease in the strength of SPC than PC but still with the given Tg value and decrease in the main chain decomposition temperature, SPC can act as a promising PEM fuel cell as normal working temperature for fuel cell is about 80ºC. Final decomposition temperature was also observed in the case of TG/DTA taken under air atmosphere at about 580ºC for PC and 520ºC for SPC but this stage is absent for nitrogen atmosphere which may be due to the decomposition of the oxidized product formed during the analysis. Total weight listed are also listed in Table 2.

3.6.4. Scanning electron microscopy (SEM)

Figure 11, a and b, show the surface morphology of polycarbonate before and after sulfonation respectively at 500 times magnification. The development of pores after sulfonation of the membranes can be observed clearly. It can be observed from Figure 1 that SPC absorb water and consequently expand to large dimensions. The high morphological modification of SPC was linked to this expansion and a swelling mechanism of PC during sulfonation with chlorosulfonic acid in air when interaction of water with the surface of SPC took place. SPC has both hydrophilic (due to sulfonic acid group attached) and hydrophobic (due to main chain of PC) zones. Water absorb due to the hydrophilic part of SPC, it pushes the non-polar domain further apart and expansion restricted by the tie molecules that connect the domain. Similar effect was observed by A.B. Affoune *et al.* [31], in their AFM study of hydrated Nafion. Kreuer [15], observed the pores in their SEM study of PEM. Uniform, adequate size and even distribution of pores ensures a desirable and efficient conductivity of protons besides a sufficiently large interfacial area between the hydrophobic and hydrophilic interface.

Table 3. Comparison of properties of SPC with Nafion.

Polymer	Thickness (μm)	IEC (meq/g)	%age Water uptake	1st Sharp Thermal decomposition under N_2 atmosphere
Nafion	130 [28]	0.91 [28]	41.0 [28]	325ºC [32]
SPC	126.60	1.15	35.54	420º

Table 3 shows the comparison of the properties of selected membrane with the properties of Nafion (mostly used proton exchange membrane for fuel cell) membrane, found in literature. The SPC has thickness close to Nation. It is an important parameter for the PEM to transport the proton through it, if the film is thin then the proton has smaller distance to travel to pass through the membrane and vice versa. In the present study, it was observed that by decreasing the thickness the strength also decreases which is not desirable. Water uptake is another interesting property for PEM to be use in hydrogen fuel cell. Humidification is the basic need for the transport of proton from one side to the other. Proton transfer through membrane is in the form of $H^+(H_2O)$, so the water content and the hydrophilic nature of the membrane facilitate the transport of proton from one side to the other. Water uptake value for Nafion is 41% as mentioned in literature [30] while it is 35% for the selected SPC membrane in this study. Water uptake value is also directly related to the IEC value of the resultant membrane. Main chain thermal decomposition of SPC shifts toward lower temperature represents the lower thermal stability of SPC as compared to PC. Main chain decomposition of the polycarbonate took place at 460˚C in air and 480˚C in nitrogen atmosphere while it becomes 400˚C and 420˚C respectively for sulfonated polycarbonate. This value is still good enough for SPC to be used in the fuel cell environment whose normal working temperature is about 80°C. Table 3 shows the sharp thermal decomposition value for Nafion is 325°C [32] which is lower than that for SPC. Present study revealed that sulfonated polycarbonate membrane can be used as a promising proton exchange membrane for fuel cell by keeping in view its properties close to Nafion.

4. Conclusion

Various properties of the sulfonated PC were measured and different techniques were utilized to establish SPC as a possible PEM candidate in FCs. The occurrence of sulfonation was confirmed using FTIR and X-ray diffraction spectroscopy. It was found that SPC developed by employing 1.0% chlorosulfonic acid result in good membranes, which have suitable IEC, DS alongwith sufficient mechanical strength. There were some variations in the results of IEC and DS due to the highly hygroscopic nature of the chlorosulfonic acid, which may change the concentration of the acid for the given experimentation. Performing the sulfonation reaction under nitrogen can eliminate this effect. It was found that PC film of mass 0.3g, sulfonated with 1.0% chlorosulfonic acid was the best SPC film with suitable IEC alongwith strength and film forming property. In the current study PC was found to be a suitable PEM candidate to be used in FCs.

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References

[1] V. Mehta and JS. Cooper, J. Power Sources **114** (2003) 32.

[2] W. Vielstich, A. Lamm, H. Gasteiger (Eds.), Handbook of Fuel Cells–Fundamentals, Technology, Applications, Wiley, (2003).

[3] HR. Allcock, AH. Michael, MA. Catherine, NL. Serguei, YZ. Xiangyang, C. Elena and W. Jamie, J. Membr. Sci., **201** (2002) 47.

[4] H.L. Yeager and A. Steck, J. Electrochem. Soc. **128**, No. 9 (1981) 1880.

[5] A.J. Appleby and F.R. Foulkes, Fuel Cell Handbook, Van Nostrand Rein-hold, New York (1989) p. 762.

[6] W. Becker and G. Schmidt-Naake, Chem. Eng. Technol. **25** (2002) 36.

[7] B. Smitha, S. Sridhar and A.A. Khan, J. Membr. Sci., **225** (2003) 63.

[8] F. Lufrano, G. Squadrito, A. Patti and E. Passalacqua, J. Appl. Polym. Sci. **77**, No. 6 (2000) 1250.

[9] M.J. Coplan and G. Gotz, Heterogeneous sulfonation process for difficultly sulfonatable poly (ether sulfone), US Patent No. 4, 413 (1983) 106.

[10] Y.S. Kim, F. Wang, M. Hickner, S. McCartney, Y.T. Hang, W. Harrison, T.A. Zawodzinski, J.E. McGrath, J. Polym. Sci. B: Polym. Phys., **41** (2003) 2816.

[11] C. Ma, L. Zhang, S. Mukerjee, D. Ofer and B. Nair, J. of Membr. Sci., **219** (2003) 123.

[12] L. Jorissen, V. Gogel, J. Kerres and J. Garche, J. Power Sources, **105**, No. 2 (2002) 267.

[13] W. Zhang, V. Gogel, K. A. Friedrich and J. Kerres, J. Power Sources, **155** (2006) 3.

[14] B. Bauer, D.J. Jones, J. Roziere, L. Tchicaya, G. Alberti, M. Casci-ola, L. Massinelli, A. Peraio, S. Besse and E. Ramunni, J. New Mater. Electrochem. Syst., **3**, No. 2 (2000) 93.

[15] K.D. Kreuer, J. Membr. Sci., **185** (2001) 29.

[16] M.V. Rouilly, E.R kotz, O. Hass, G.G.Scherer and A. Chapiro, J. of Membr. Sci., **81** (1993) 89.

[17] T. Yamaki, M. Asano, Y. Maekawa, Y. Morita, T. Suwa, J. Chen, N. Tsubokawa, K. Kobayashi, H. Kubota and M. Yoshida, Radiat. Phys. Chem., **67** (2003) 403.

[18] F.N. Buchi, B. Gupta, O. Haas and G.G. Scherer, Electrochim. Acta, **40**, No. 3 (1995) 345.

[19] S. Hietala, M. Koel, E. Skou, M. Elomaa, and F. Sundholm, J. Mater. Chem., **8**, No. 5 (1998) **1127**.

[20] B. Smitha, S. Sridhar and A. A. Khan, Macromolecules, **37** (2004) 2233.

[21] S.R. Samms, S. Wasmus and R.F. Savinell, J. Electrochem. Soc., **143**, No. 4 (1996) 1225.

[22] Q.H. Guo, P.N. Pintauro, H. Tang and S. O'Connor, J. Membr. Sci., **154**, No. 2 (1999) 175.

[23] R. Carter, R. Wycisk, H. Yoo and P.N. Pintauro, Electrochem. Solid State Lett., **5** No. 9 (2002) A195.

[24] R.W. Kopitzke, C.A. Linkous and G.L. Nelson, Polymer Degradation and Stability, **67** (2000) 335.

[25] W.J. Lee, Y.J. Kim and S. Kaang, Synthetic Metals, **113** (2000) 237.

[26] T.Y. Chen and J. Leddy, Langmuir, **16** (2000) 2866.

[27] A. Clearfield and J.A. Stynes, J. Inorg. Nucl. Chem., **26** (1964) 117.

[28] C. Yang, S. Srinivasan, B. Bocarsly, S. Tulyani and J.B. Benziger C, J. Membr. Sci., **237** (2004) 145.

[29] N. Gunduz, Synthesis and Characterization of Sulfonated Polyimides as Proton Exchange Membranes for Fuel Cells , Ph.D. Thesis, VPI & SU, 2001.

[30] S.R. Samms, S. Wasmus and R.F. Savinell, J. Electrochem. Soc., **143** (1996) 1498.

[31] A.M. Affoune, A. Yamada and M. Umeda, Journal of Power Sources, **148** (2005) 9.

[32] N. H. Jalani, K. Dunn and R. Datta. Electrochimica Acta, **51** (2005) 553.