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Fabrication of solid proton conducting high performance composite membranes for the application of hydrogen fuel cells

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ABSTRACT

The hydrogen fuel cell advantageously used as clean energy generators due to significant technological and economical advantages. Highly efficient and mechanically stable proton exchange membranes are demanded for high temperature fuel cells (FCs) working conditions. To this end, we have fabricated inorganic solid proton conductors as energy transport carrier components in composite membranes and tested for their performance in high temperature H_2–aerated hydrogen fuel cells. The as-developed system exhibited higher activity up to maximum power density of ca. 27.714 mW/cm^2 and current density of ca. 117.7 mA/cm^2 at a cell voltage of 0.354 V at 60°C working temperature. In addition, the enhanced mechanical stability was observed at different operating temperatures and pressures on the fuel cell performance of a composite membrane. Their mechanical stabilities were also confirmed by tensile mechanical testing mechanism, which showed excellent results for their mechanical strength. The obtained outstanding performance of hydrogen fuel cell membranes attribute toward the construction of composite membranes with incorporation of solid inorganic species as proton conductors in the matrix.

Keywords: Hydrogen fuel cell; Solid proton conductors; Proton exchange membrane; High temperature fuel cells; Hydrogen fuel cells

1. Introduction

In line with the estimates of some oil companies, the production of conventional fuels will peak sometime around the end of the next decade, and then decline [1]. With increasing world population and environmental pollution, there is needed to look for alternate sources to energy to meet the increasing demand for cleaner fuel. Fuel cell, which gives direct conversion of chemical energy stored in a fuel directly to electrical energy, is an attractive alternative as a source of electrical energy [2]. Among those, hydrogen fuel cells have been used as power sources in portable electrical devices and electrical vehicles. This research puts new demands for the materials being used in such kind of fuel cells, i.e. membrane materials owing hydrated perfluorosulfonic polymer such as Nafion.

The membranes to be used in hydrogen fuel cells must show superior performance in fuel cells devices operating at moderate temperature (<90°C) and with relative high humidity with pure hydrogen as a fuel. Hydrogen fuel cells incorporate a polymer membrane and operate at relatively low temperature and exhibit high power density. The main hindrance to the successful commercialization of this type of fuel cell is the high cost involved with the catalysts used, and the electrolyte used [3]. These limitations have oriented interests and strategies for developing of alternative proton exchange membranes for hydrogen fuel cells. The tuning of such membranes by the fabrication of small inorganic particles as proton conducting species, i.e. sulfophenylphosphonates introduced major improvement in their performance toward hydrogen fuel cells in pressurised environment and relatively higher temperatures up to 140°C.

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The common types of electrolyte used till date for proton exchange membranes are the perfluorinated membranes, mainly Nafion. However, as mentioned earlier, Nafion suffers from remarkable drawbacks of high cost (~1000 $/m), low performance at high temperature and low humidity, and are not environmentally friendly [4,5], and these problems must be addressed for successful market introduction. Preparation of Nafion involves use of fluorine based technology which is non friendly to the environment [3]. With these drawbacks involving perflourosulfonic acid polymeric electrolytes, some modification in the perflourosulfonic acid membranes to improve their water retention properties, or opting for non fluorinated polymeric electrolytes or designing inorganic-organic composite membranes was required [3].

Composite Nafion membranes were prepared and tested to improve the properties. Composite Nafion membranes were prepared with silicon dioxide which improves the water retention property of the membrane. These membranes were tested in a fuel cell operating at 80°C–140°C. With incorporation of silicon dioxide into Nafion, the conductivity of the membranes at elevated temperatures is improved. Incorporation of titanium dioxide into Nafion also improved the water retention property of Nafion [6]. Considerable research and advances in the area of polymer fuel cell electrolytes have been made over the past decade. Nafion/HPA (heteropolyacid) composite membranes were prepared and tested at high temperature (90°C–120°C). The inorganic heteropoly acids tested were phosphotungstic acid, phosphomolybdic acid and silicomolybdic acid. It was found that the inorganic additives improved the conductivity of the Nafion at high temperature, but heteropoly acids are highly soluble in water [7].

Blending of Nafion with another polymeric material was also tried. Nafion/sulfonated poly(aryl ether ketone) (SPAEK) composite membranes was prepared by blending [8], The addition of SPAEK offered better mechanical properties to the composite material than bare Nafion. The mechanical strength increased with increasing SPAEK content. SPEAK acted as a methanol barrier in a direct methanol fuel cell (DMFC). However, the proton conductivity of the blend membranes was lower than those of Nafion in a DMFC. To address the problem of high cost of perflourinated membranes and their unfriendly nature toward the environment, alternative membranes based on fluorine free hydrocarbon ionomers such as polyvinyl alcohol [9], polyimide [10], polyethersulfone [11] and polyphosphazine [12], were reported. Sulfonated poly(ether ether ketone) (SPEEK) was reported to have good thermal stability and mechanical strength [4].

These SPEEK membranes are quite interesting toward energy conversion devices. The SPEEK membrane is more than three times cheaper than Nafion. These SPEEK membranes were found to possess low conductivity in a H_2–air fuel cell [13]. Composite SPEEK membranes were also prepared and tested to improve the conductivity, prepared composite SPEEK membrane by blending SPEEK with boron orthophosphate (BPO_4) for DMFC application [14]. SPEEK/functionalized silica composite silica composite membranes were also prepared and their proton conductivity tested [15]. In another study, sulfonated polyether ether ketone composite membrane using tungstosilicic acid (SiWA) supported on silica–aluminium oxide (SiO_2–Al_2O_3) were prepared and tested for water uptake and proton conductivity. SiWA was supported on the stable composite oxide structure so that it became insoluble in water. The presence of inorganic proton conducting fillers led to both high water uptake and proton conductivity (maximum value of proton conductivity = 6.1×10^{-2} S cm^{-1}). Low methanol permeability values recorded for the membranes tipped them as a very promising material to be used in DMFC [16].

The incorporation of heteropoly acids into the SPEEK matrix was first introduced previously by our group. [17] This resulted in the improvement of the proton conductivity at elevated temperature and also the thermal stability of the membranes improved. But heteropoly acids are highly soluble in water. In earlier studied physical characteristics of composite SPEEK membranes, heteropoly acids as tungstophosphoric acid (TPA) or molybdophosphoric acid (MPA) were first supported onto Y-zeolite or MCM-41. Hence, SPEEK/heteropoly acids loaded MCM-41 membranes showed proton conductivity in the range (6.7–8.1) × 10^{-3} S/cm with water uptake of 140°C. SPEEK/heteropoly acids loaded Y-zeolite exhibited a proton conductivity of 7.8 × 10^{-3} S/cm at 140°C [3,18].

In present work, the advancement in composite SPEEK membranes were implemented by incorporating conducting powered materials consisting of TPA and MPA based Y-zeolite. The solid proton conducting material is first synthesized by supporting TPA and MPA onto Y-zeolite. Then this material is incorporated into SPEEK polymer to make the membrane. The membrane electrode assemblies were prepared using these membranes and finally tested for their performance in H_2/air fuel cell test station. The mechanical strength testing of these membranes was carried out using Instron 5567 to see the effect of incorporation of solid proton conducting fillers into SPEEK matrix on the tensile mechanical properties.

2. Experimental setup

2.1. Synthesis of heteropoly acids loaded onto Y-zeolite

Analytical grade TPA and MPA were used as received from Fluka chemicals. The loading of the heteropoly acids onto Y-zeolite was carried out according to the method of Mukai et al. [19] with some modifications. It has been studied earlier that 40% loading of heteropoly acids (TPA and MPA) on Y-zeolite respectively, gives the optimal loading for high proton conductivity and low leaching. [18] Calculated amount of heteropoly acids was dissolved in distilled water. To prevent the heteropoly acids from decomposing in the solution, drops of 10% V/V HCl solution were added. Measured amount of Y-zeolite was then added to the contents. This solution was then given ultrasonic treatment for 30 min to ensure good mixing. Thereafter, the contents in the beaker were dried first by placing it on a heating plate with magnetic stirring. The contents were heated continuously at plate temperature of 80°C and stirred. To remove excess moisture that was still present, the dried material is meshed to powder. Then the powder was placed in a programmable oven at a temperature of 200°C for 6 h. The ramp rate of the oven was set at 1°C/min for raising the temperature from ambient to 200°C. The beaker was then removed and allowed to cool inside a dessicator.

2.2. Synthesis of composite sulfonated poly (ether ether ketone) membranes

SPEEK of IEC 1.68 was obtained from the Fumatech Company, Germany, for the purpose of preparing SPEEK and composite SPEEK membranes. About 100 ml of casting solvent, Dimethyl acetamide purchased from Aldrich, was taken in a 250 ml beaker, and placed on the heating plate magnetic stirrer. Measured amount of solid proton conducting powder (MPA loaded Y-zeolite or TPA loaded Y-zeolite) was added to the solvent slowly with stirring. Solution casting technique is adopted to prepare the membranes. Calculated amount of SPEEK was then dissolved in the solvent. The initial total solid content in the solution was kept around 3%–5% to form homogeneous solution. The solvent in the solution is then evaporated on a heating plate with continuous stirring. At some point a viscous solution is formed, and the solution was poured onto the glass plate and spread uniformly using doctor's knife. The membranes were dried overnight at room temperature. Then the membranes were dried in an oven in steps till 110°C, to completely evaporate the solvent. The membrane was removed from the glass plate by soaking in deionized water in a water bath. The membrane was washed thoroughly, and then boiled in 0.5 M H_2SO_4. The membrane was washed and saturated by boiling it in water.

2.3. Preparation of membrane electrode assembly

Calculated amount of catalyst was taken in the beaker of spray gun, wetted with water and then stirred with the help of magnetic stirrer and bead. Next, the catalyst was solvated by ethanol, and stirred. Measured amount of Nafion solution was then added to form catalyst ink. The catalyst ink was stirred with help of magnetic stirrer, then in ultrasonic bath for few minutes. The ink was then sprayed evenly on the substrate, and then left to dry at room temperature. Then it was dried in a programmable oven at 70°C for 30 min, to evaporate the water and solvent. The membrane was sandwiched in between two electrocatalyst layers and we get membrane electrode assembly, so all the MEA samples had the same electrocatalyst loading.

2.4. Fuel cell testing of membrane electrode assemblies

The fuel cell testing of the membrane electrode assemblies (MEA) prepared above was carried out in a fuel cell testing station purchased from Arbin Instruments, USA. The MEA was fitted into the cell in between the graphite plates. Flow rate of the chiller water was maintained greater than 100 ccm. The gases, hydrogen, nitrogen and air, are supplied with an inlet pressure of about 60 psig. Operating pressure of 20 psi and operating temperature of 60°C (with full humidification) were maintained. The results of tests are collected in a form, which was interfaced with the Excel to give polarization curves in desirable form.

2.5. Tensile mechanical testing of polymer membranes

The tensile tests were performed on the Instron 5567 tensile testing machine at 25°C. For this purpose membrane samples were pre-treated and cut into dog bone shape according to the standard ASTM D638 type V procedure. The gauge length was 25 mm and crosshead speed was 10 mm/s. The mechanical parameters are reported based on an average of three samples. The yield stress, stress at break and strain at break was studied as function of polymer content. The thickness of the dog bone samples on the average was 180 microns. The membrane samples with various compositions were tested, with 3 specimens for each. The membrane samples were: pure SPEEK, 20% and 40% loading of MPA-Y zeolite onto SPEEK, 20% and 40% loading of TPA-Y zeolite onto SPEEK. The mechanical properties of the composite samples were compared with that of pure SPEEK.

2.6. Results and discussion

The morphology of composite membranes Fabricated with solid proton conductors was analyzed by scanning electron microscopy (SEM) analysis, presented in Figs. 1(a)–(d). It can be observed from SEM images that the composite membrane shows a layered morphology with substantial uniform dispersion of solids fabricated into the composite polymer matrix with no or negligible agglomeration, which can be attributed to the large sizes of the inorganic proton conductors. This analysis confirms the uniform incorporation of proton conductors to construct the high performance Fuel cells (FCs) membranes.

The fuel cell performance tests of as-prepared composite SPEEK membranes were done and compared with the performance of pure SPEEK membrane. The proton conductors loaded onto SPEEK matrix in the ratio of 40:60. These membranes are then tested in the form of MEA. The performance of each membrane in a hydrogen-air fuel cell was then compared with that of pure SPEEK membrane at 60°C and 20 psi. For the trend, 20% loading of solid proton conductors on Y-zeolite was also tested. The performance of polymeric membrane electrolytes for fuel cell application was given by the polarization curves, in which output voltage was plotted against the current density (see Figs. 2 and 3.).

From Fig. 2 we observe that at a fixed voltage, the power density obtained for membranes with different percentages of proton conductor (composite TPA-Y zeolite) loading increases with increase in degree of inorganic proton conductor loading. The composite SPEEK membranes

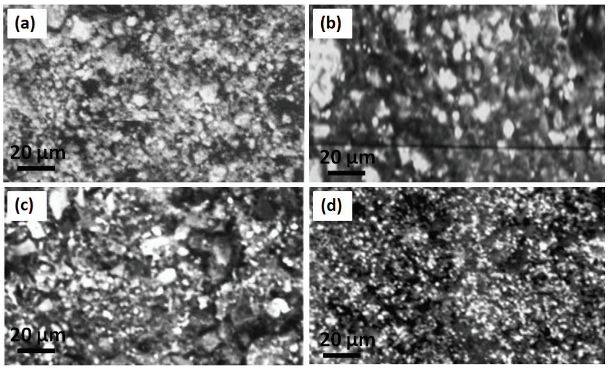

Fig. 1. SEM images for all the composite membranes ((a) and (b)) 20% TPA-Y/SPEEK and 40% TPA-Y/SPEEK respectively, ((c) and (d)) 20% MPA-Y/SPEEK and 40% MPA-Y/SPEEK respectively.

exhibited better fuel cell performance as compared with pure SPEEK membrane in terms of power density obtainable at any voltage and also the maximum power density achievable. Similar observations were made for composite MPA-Y zeolite as proton conductor when it is incorporated into SPEEK matrix with varied degrees of loading (Fig. 3.). Table 1 gives the numerical values of the maximum current densities obtained at 0.1 V for each of the membranes, and the maximum current densities.

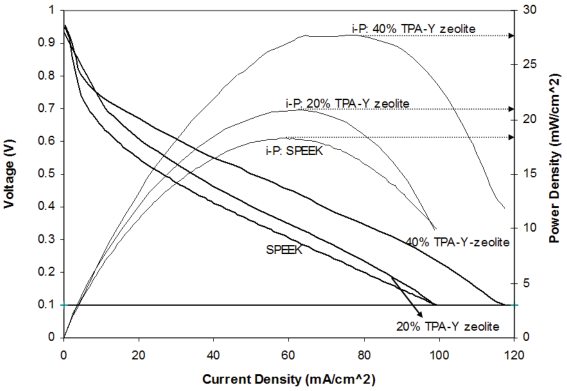

Fig. 2. Polarization curves and plots of power density vs. current density for different percentages of TPA-Y-zeolite loading into SPEEK matrix [Operating conditions: Anode flow (H_2) = 100 sccm, cathode flow (air) = 200 sccm, T_{cell} = $T_{humidifiers}$ = 60°C, Pressure = 20 psi].

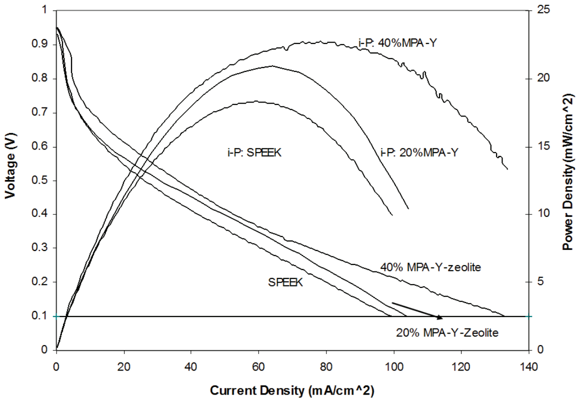

Fig. 3. Polarization curves and plots of power density vs. current density for different percentages of MPA-Y-zeolite loading into SPEEK matrix [Operating conditions: Anode flow (H_2) = 100 sccm, cathode flow (air) = 200 sccm, T_{cell} = $T_{humidifiers}$ = 60°C, Pressure = 20 psi].

The maximum power densities and maximum current densities of composite SPEEK membranes are higher than of pure SPEEK membrane. We observed that as the loading of composite solid proton conductor is increased in the matrix, the maximum power density and maximum current density also increased for each case. This was due to the presence of solid proton conductors in the matrix that enhances the performance of the fuel cell. Forty percent loading of solid proton conductors (MPA-Y zeolite) have higher values of maximum current densities and maximum power densities (better fuel cell performance) than corresponding values for 20% loading. This was also due to the higher percentage of solid proton conductors in the matrix for the case of 40% loadings. Higher loading (>40%) of solid proton conductors onto SPEEK were not tested as the membranes become very much brittle to be used as electrolyte in the fuel cell assembly. The proton conductivity was found to increase with the increase in the degree of loading of solid proton conductors in the SPEEK. As proton conductivity was increased, we expect better performance of fuel cell membranes.

The enhanced performance of as-developed system can be explained as, in composite membranes loaded with solid proton conductors, the hydrophobic/hydrophilic nano-separation occurs among water molecules. The aggregates of sulfonic acid functional groups formed to produce hydrophilic domains. The hydration of these domains lead to proton conducting phenomenon with solid proton conductors as proton charge carriers from inner space charge layers via dissociation of acidic functional groups. So as, the hydrophilic domains in present system favors the transportation of protons and water molecules. Whereas, the hydrophobic domains provide them structural and morphological stabilities, those were also tested in present studies by means of tensile strength.

Moreover, the study to evaluate the tensile mechanical properties of SPEEK and heteropoly acids loaded Y-zeolite/SPEEK composite membranes have been carried out. The uniaxial tensile properties of the membranes were studied as a function of the filler-to-matrix ratio. The stress-strain response of the membranes was measured as a function of the filler content. The introduction of the solid fillers to enhance proton conductivity leads to the deterioration in the mechanical performance compared with unfilled SPEEK.

Table 1
Maximum current density and maximum power density for different composite membranes

Material (average thickness = 185 microns)	Maximum current density (mA/cm^2) at 0.1 V	Maximum power density (mW/cm^2)	Voltage at maximum power density (V)
Pure SPEEK	99.452	18.318	0.309
20% TPA-Y/SPEEK	98.976	20.844	0.329
40% TPA-Y/SPEEK	117.707	27.714	0.354
20% MPA-Y/SPEEK	104.212	20.904	0.327
40% MPA-Y/SPEEK	133.501	22.702	0.311

The comparison of the mechanical tensile properties of pure SPEEK membrane and composite membrane with 20% and 40% loading of solid proton conductors (TPA-Y zeolite, 40:60) onto SPEEK matrix was investigated and provided in Fig. 4. All the membranes were pre-treated before they were tested for mechanical strength. The pure SPEEK has a lengthy plateau region and that indicates the plastic nature of the pure membrane. There is decrease in the plateau region of the material for 20% loading. The incorporation of inorganic proton conductive fillers in the matrix introduces brittleness into the material. With the increase in content of inorganic filler, the plasticity and strength of the material is decreased. The plastic region of the composite material containing 40% filler content is even more brittle than material containing 20% fillers. So there is a transition from ductile to brittle behavior with incorporation of fillers into the matrix.

Similar results were obtained for composite membrane with 20% and 40% loading of solid proton conductors (MPA-Y zeolite, 40:60) onto SPEEK matrix (Fig. 5.). From the results obtained from stress strain curves, the yield stress is plotted vs. filler fraction for both types of solid proton conductors. We observe that the yield stress is reduced as the fraction of filler is increased in the matrix (Figs. 6(a)–(d)). It is observed that the addition of filler did not reinforce the initial modulus

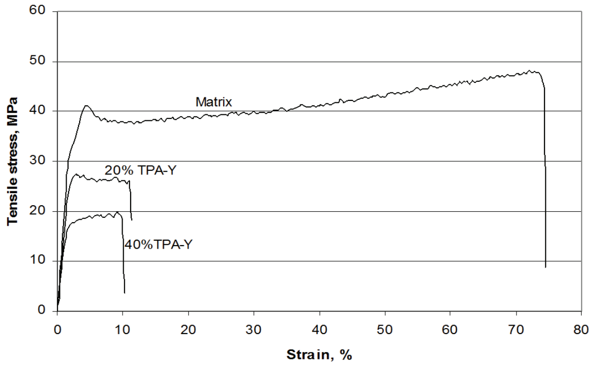

Fig. 4. Stress-strain curves of SPEEK and composite SPEEK (TPA-Y-zeolite/SPEEK) films, illustrating the effect of the filler (TPA- Y zeolite) to matrix ratio on the tensile properties of the membrane.

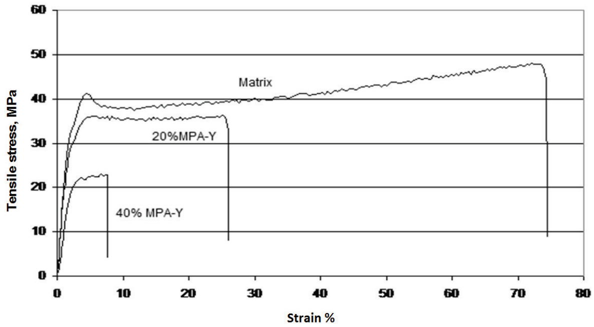

Fig. 5. Stress-strain curves of SPEEK and composite SPEEK (MPA-Y-zeolite/SPEEK) films, illustrating the effect of the filler (MPA- Y zeolite) to matrix ratio on the tensile properties of the membrane.

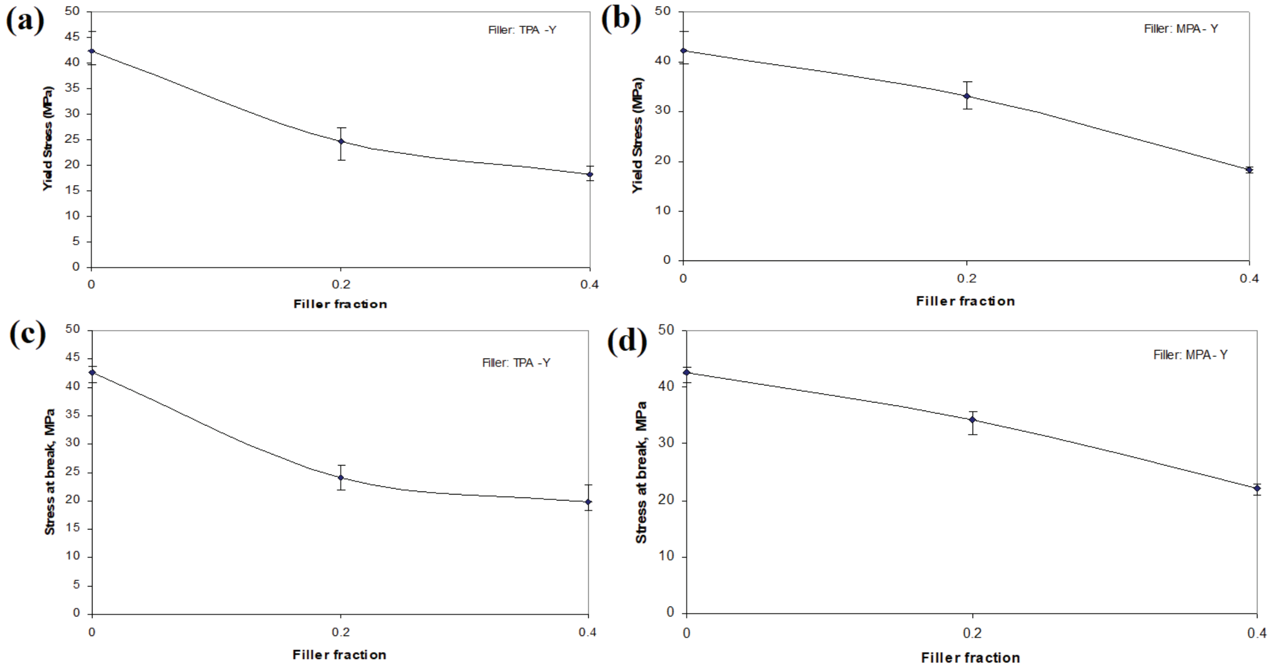

Fig. 6. (a) Effect of filler (TPA- Y zeolite) to matrix ratio on the yield stress of SPEEK and composite SPEEK, (b) Effect of filler (MPA- Y zeolite) to matrix ratio on the yield stress of SPEEK and composite SPEEK, (c) Effect of filler (TPA- Y zeolite) to matrix ratio on the stress at break of SPEEK and composite SPEEK, (d) Effect of filler (MPA- Y zeolite) to matrix ratio on the stress at break of SPEEK and composite SPEEK.

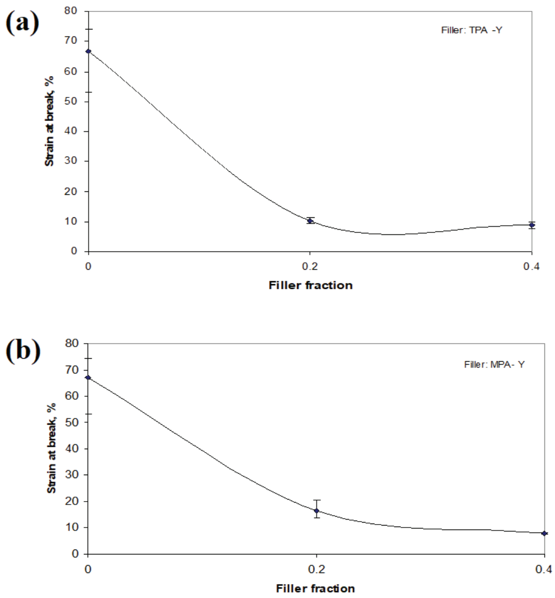

Fig. 7. (a) Effect of filler (TPA- Y zeolite) to matrix ratio on the strain at break of SPEEK and composite SPEEK, (b) Effect of filler (MPA- Y zeolite) to matrix ratio on the strain at break of SPEEK and composite SPEEK.

of the matrix. Three samples were chosen for each type at each filler percentage and studied for their tensile mechanical strength. The stress at break and the strain at break are plotted vs. filler fraction for both types of solid proton conductors from obtained stress strain curves results (Figs. 7(a) and (b)).

The stress at break and the strain at break decreased as the fraction of filler (inorganic composite proton conductors) in the matrix are increased. The poor mechanical tensile performance exhibited by the composite SPEEK membranes is probably due to poor or non-existent adhesion between the rigid particulate filler (heteropoly acids-Y zeolite) and the polymer matrix (SPEEK).

The results of the mechanical characterization obtained are in agreement with studies conducted earlier for similar systems. Valencia et al. [20] investigated the mechanical tensile properties of composite SPEEK membranes using BPO_4 as fillers [21]. The percentages of BPO_4 in the matrix were varied between 15%–50%. They reported that that the mechanical properties deteriorated with the introduction of inorganic BPO_4 in the SPEEK matrix. They attributed this to the poor adhesion between the rigid particulate filler and the polymer matrix. Brittleness was introduced in the composite materials as the fillers hindered the chain orientation process.

It is well-documented that membranes have potential usefulness in water desalination and treatment systems. So far, the trivial ceramic based membranes have been used for these kinds of applications, but currently developed membranes have worth to replace the ceramic-based membranes due to their flexible nature. Meanwhile, present composite membranes with loading of heteropoly acids have also removed the drawbacks of their own class of groups by improving the hydrophilic characteristics. The overall nature of these proton conducting composite membranes highly orient their potential use in both the directions such as energy and environmental sections for water desalinations by enhanced conductivities and removing the dissolved ions and organics more favorably, respectively in twined directions.

3. Conclusion

The composite SPEEK membranes with different loadings of solid proton conductors were successfully tested for their fuel cell performance. The composite membranes exhibited better fuel cell performance than the pure SPEEK at a specified of condition in terms of power density and I/V characteristics. This means that the conductivity of the membranes is enhanced with the addition of these solid proton conductors. The ratio of heteropoly acids to Y-zeolite, is kept 40:60 as earlier study has indicated this percentage for optimal loading for maximum conductivity and minimum leaching. This composite material combines the high thermal and structural stability of Y-zeolite with outstanding conductivity of heteropoly acids. 20% loadings of these composite conductors onto SPEEK matrix gave improved fuel cell performance than obtained with pure SPEEK. Still better performance in fuel cell conditions is obtained with 40% loadings of these conductors at 60°C and 20 psi pressure.

The results of the mechanical properties of the membrane showed that some brittleness was introduced in the structure with the incorporation of fillers into the matrix. The strength of the material decreased with the increase in filler content. However, this will not affect the overall performance of the fuel cell as in the practical operation the membranes and MEAs are sandwiched between the strong bipolar plated. These membranes have potential to be considered as an alternative to the commercially available membranes for hydrogen fuel cell application.

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