



Proton Conductivity and FTIR Studies of Methanesulfonic Acid (MSA) Incorporated Polyacrylamide based Composite Solid Polymer Electrolyte.

Sumathi S.^{a*}, Sethuprakash V.^b, W. J. Basirun^c, I. Zainol^d

^{a,b,d}Department of Chemistry, Sultan Idris Education University, 35900 Tanjong Malim, Perak, Malaysia.

^cDepartment of Chemistry, University Malaya, 50603 Kuala Lumpur, Malaysia.

^eInstitute of Nanotechnology and Catalysis (NanoCat), University Malaya, 50603 Kuala Lumpur, Malaysia.

^aEmail: sumathi2311@gmail.com

Abstract

A new class of Composite Solid Polymer Electrolyte Membrane (CSPE) of Polyacrylamide (PAAm) with Methanesulfonic acid (MSA) was synthesized. The composite membranes were thoroughly characterized by FTIR and proton conducting performance. The highest proton conductivity of $1.17 \times 10^{-6} \text{Scm}^{-1}$ was observed at room temperature with the loading of 5M of MSA into the polymer matrix. FTIR spectroscopy was used to study the mechanism involved in the protons transfer in the membranes by referring the characteristic shifts of the absorbance bands of C=O and N-H₂. Thermal parameters such as the glass transition temperature (T_g) and the melting point (T_m) of the polymer membrane with the highest proton conductivity were measured by TGA and DSC. The morphology of the PAAm-5M MSA was observed by FESEM. The valued merits on the proton conductivity, thermal stability and easy synthesis promise the new membranes to be good alternative as CSPE for electrochemical devices.

Keywords: Composite Solid Polymer Electrolytes; FTIR; Methanesulfonic acid; Polyacrylamide; Proton Conductivity.

* Sumathi S.

E-mail address: sumathi2311@gmail.com.

1. Introduction

The research and development effort has been made throughout the world on solid polymer electrolyte (SPE) since Wright [1] discovered that the complex of PEO and alkaline salts in 1973. The use of a SPE in batteries, fuel cells and other electrochemical device eliminates the need for containment of the liquid electrolyte which simplifies the cell design, as well as improves safety and durability [2]. However, development of SPE capable of high ionic conductivity and good mechanical properties are the key problems for the R&D of SPE. Although studies showed that formation of networks by irradiation or chemical cross-linking can greatly improve the mechanical properties [3] but it may lead to excessive rigidity of the polymer chain with a consequent decay in the ionic conductivity. Alternatively, a new strategy, whereby the ceramic powder [2,4], organic acid [5], and organic/inorganic fillers[6] were dispersed directly into the polymer hosts to improve the mechanical strength and ionic conductivity of SPE. Incorporated of these particles physically into the host polymers produced the composite solid polymer electrolytes (CSPEs).

The addition of inorganic fillers such as silica (SiO₂) [7], TiO₂ [8,9], Al₂O₃ [10] to polymer films improved the physical strength as well as the increase in ionic conductivity. The maximum ionic conductivities of 10⁻³ to 10⁻⁴ Scm⁻¹ were reported in many studies [7-10]. A great enhancement in the conductivity as well as the mechanical properties of the lithium salt-PEO composite electrolytes was reported by using the combined action of a large surface and the Lewis acid character of the ceramic additive[11]. Addition of some ceramic could suppress the decomposition of polymer electrolyte towards the cathode thus showing an improvement in charge/discharge efficiency [12]. Study also showed synthesizing composite solid polymer electrolyte by incorporating of organic acid resulted in increased Tg and enhance membrane hydrophilicity, bringing about a substantial gain in proton conductivity [13].

In the present study, the new composite solid polymer electrolyte (CSPE) was prepared by using methane sulfonic acid (MSA) and polyacrylamide (PAAm) to improve the characteristics of the electrolyte. Various experimental parameters affecting the characteristics of the polymer membrane were investigated including: proton conductivity, thermal stability of the CSPE membrane employing the thermal gravimetric (TGA) analysis, FTIR and morphology study with FESEM.

2. Experimental

2.1 Synthesis of PAAm-MSA composite membranes.

The PAAm-MSA composite membranes were synthesized by using Polyacrylamide (Polyscience Inc., Sigma-Aldrich) and methane sulfonic acid (> 99.5%, Sigma-Aldrich) as the starting materials. In detail, 1.25g of solid PAAm was stirred continuously with 50ml of distilled water at room temperature to form homogenous solution. The solution obtained was divided into two portions and under the vigorous stirring; MSA (9.6g) was added to the above solution separately. The reagent solutions were kept aside in a sealed bottle at room temperature for two weeks. White elastic gel membranes were produce. The resultant products were then filtered and soaked in deionized in the petri dish to raise the membranes. The deionized water was changed every day for three days.

After rising with deionized water, the membranes were dried in the oven at 60°C for 48 hours to obtain the final PAAm-MSA (4M) composite solid polymer disc electrolyte which was brownish in color. These processes were continued with 12.0g 14.4g and 16.8g to produce composite membranes with various concentration of MSA (5M to 7M) as seen in Figure 1.



Figure 1: Composite Solid Polymer Membranes (a) White elastic gel membrane before dried
(b) 4M MSA (c) 5M MSA (d) 6M MSA (e) 7M MSA

2.2 Proton conductivities of Composite Solid Polymer Electrolyte Membranes.

Electrochemical impedance spectroscopy (EIS) was used to characterize the proton conductivity of the PAAm-MSA composite solid polymer electrolytes membranes at room temperature. The thicknesses of the resulted membranes were measured using micrometer screw gauge and the average thickness of each membrane was used in the calculation of proton conductivity. The composites polymer electrolyte membrane was sandwiched between the two disc-like stainless steel electrodes (20mm in diameter). The proton conductivity of the membrane was characterized with A.C impedance spectroscopy using potentiostat/galvanostat, Autolab PGSTAT 30 system (Eco Chemie, B.V. Netherlands). A frequency response analyzer (FRA) software module installed in a computer interfaced to the potentiostat/galvanostat was used to control, run and analyze the EIS data. The proton conductivity ($\sigma / S \text{ cm}^{-1}$) was calculated from the bulk electrolyte resistance value (R_b), from the intercept at the real impedance axis in the Nyquist plot. The proton conductivity of the membrane was determined using the equation, $\sigma = t / R_b A$, t = is the thickness of the film and A is the effective membrane electrode contact area.

2.3 Fourier Transform Infrared studies

Fourier Transform infrared (FTIR) spectra were recorded on a computer interfaced Perkin-Elmer System 2000 series spectrophotometer (USA) with a wave number range of 400-6000 cm^{-1} . This analysis technique provided information regarding the molecular structure and chemical bonding of materials. FTIR was used to study the mechanism involved in the protons transfer in the membrane.

2.4 Thermal Analysis

Thermogravimetric analysis (TGA) is the thermal analysis used to characterize the PAAm-methanesulfonic acid

composite solid polymer electrolyte. The PAAm-MSA membrane with highest ionic conductivity was used to determine the thermal stability of material as well as their compositional properties. TGA measures the amount and rate of change in the mass of the membranes as a function of temperature. TGA was carried out using Mettler-Toledo TGA/SDTA 851^o. The experiment procedure consisted of the heating the samples in flowing nitrogen (99.99% purity, 40ml min⁻¹) at a heating rate of 10^oCmin⁻¹ from 20^oC to 550^oC. TGA measurements provided valuable information that was used to select materials for end-use application.

The PAAm-MSA composite with the highest ionic conductivity was also subjected to Differential Scanning Calorimetry (DSC) test. This technique was used to study the thermal transitions of the synthesized electrolyte. The melting point of the membrane was detected from the DSC curve. Other parameters, such as the temperature of the decomposition of the samples and the glass transition temperature, T_g, were also detected from the DSC curve. The thermal behavior of the electrolyte membranes was studied utilizing Mettler Toledo DSC 822^o in a temperature range 20^oC to 550^oC with a scan rate of 10^oCmin⁻¹ under a constant flow(40ml min⁻¹) of nitrogen gas to avoid any contact of atmospheric moisture.

2.5 Other Characterization

The morphology of the PAAm-MSA composite membrane with the highest ionic conductivity was captured with a FEI Quanta 200 emission scanning electron microscope (FESEM).

3. Results and Discussions

3.1 Proton conductivities of PAAm-MSA Composite Solid Polymer Electrolyte Membranes.

PAAm-MSA composite membranes with various concentration of MSA were synthesized and evaluated via conductivity. Figure 2 with an extension of the frequency range 10⁶-10Hz, shows the Nyquist plots at room temperature of CSPE with different concentration of MSA. The values of the bulk resistance, R_b, average thickness of the membranes, average radius of the membranes and the calculated proton conductivities of the PAAm-MSA CSPE are tabulated in Table 1. The room temperature conductivities of the CSPEs are shown in Figure 3. It is evident that the concentrations of MSA at 5M is an optimal condition in generating the highest proton conductivity of 1.17 x 10⁻⁶Scm⁻¹ and gradually decrease to lower values as the concentration of MSA increased to 6M and 7M. However, this value is lower than that the ionic conductivity obtained by the PAAm-MSA gel polymer electrolyte with the highest conductivity of 7.0 x 10⁻¹ S cm⁻¹ [14]. Therefore, the state of hydration has a significant effect on the conductivity of the polymer.

In the composite membranes, after the membrane is dried at 60^oC, its volume shrinks considerably when the sulfonic acid molecules are completely trapped inside the PAAm-sulfonic acid matrix. Thus, we hypothesize that H₂O molecules did not involve in the proton transport and conductivity only from the proton transfer to the adjacent sulfonic acid molecules along the hydrogen bond (Figure 4). The removals of the H₂O bring closer the sulfonic acid molecules to the PAAm network bones to form hydrogen bonds with electronegative atoms such as O and N in carbonyl and amide groups abundant in the PAAm frame work. These hydrogen bonds serve as the pathways for proton transfer to the free sulfonic acid groups as well as within the framework. The sulfonic

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Table 1: The physical properties, R_b values and the proton conductivity of the CSPEs with different concentration of MSA

Concentration(M)	Thickness/t(cm)	Radius/r(cm)	R _b /Ω x 10 ³	Conductivity(S _{cm} ⁻¹)
4	0.129	1.05	209	1.78 x 10 ⁻⁷
5	0.112	1.075	26.40	1.17 x 10 ⁻⁶
6	0.1065	1.25	83.50	2.60 x 10 ⁻⁷
7	0.131	1.15	126.33	2.50 x 10 ⁻⁷

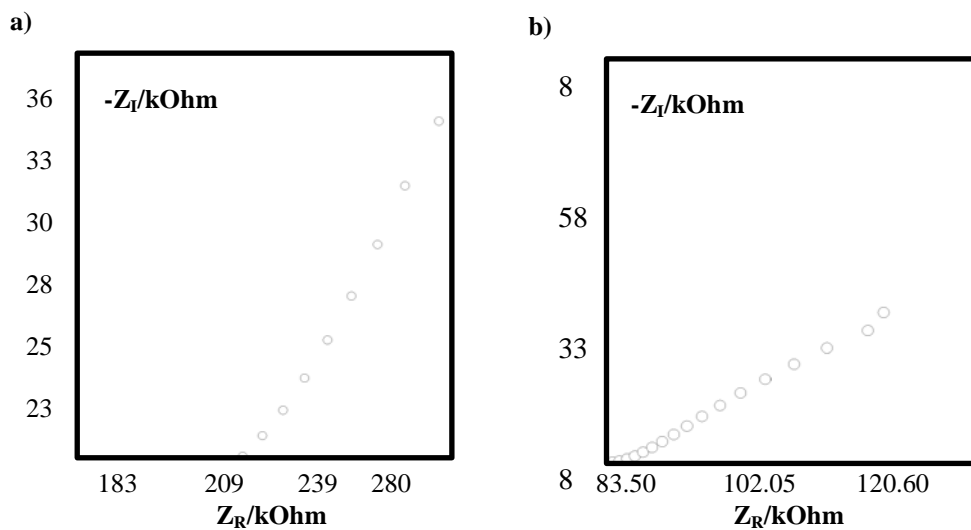


Figure 2: The Nyquist plots for PAAm CSPE with a) 4M and b) 6M of MSA

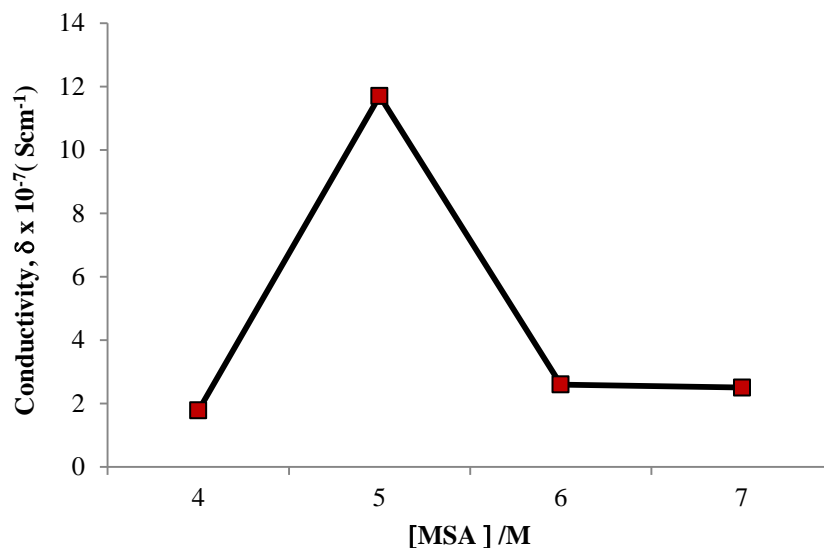


Figure 3: Variation of conductivity of PAAm-MSA CSPE as the function of MSA concentration

In this study, the membranes with higher sulfonic acid loading showed rigidity indicating limited number of free sulfonic acid presences in the membranes which reduced the proton conductivity of the synthesized membranes. It could be either:

- 1) The number of sulfonic acid molecules caged in the polymer matrix are less or
- 2) Increase in the number of formation of hydrogen bonds between sulfonic acids and polymer which reduce the number of free sulfonic acids

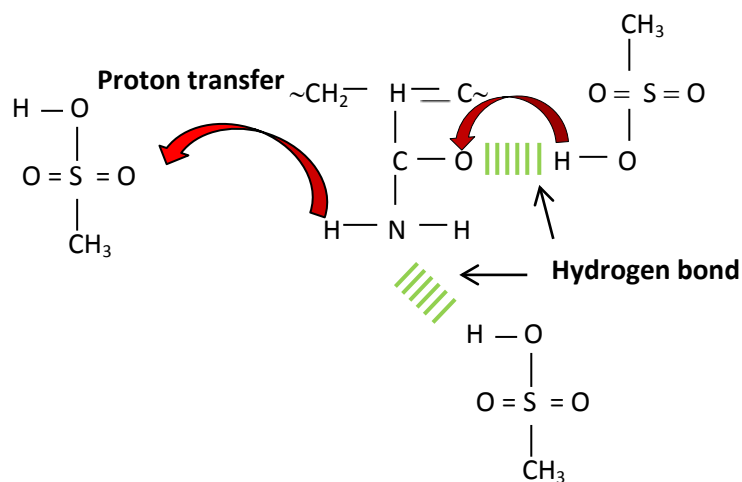


Figure 4: Protons Transfer by the formation of hydrogen bonds

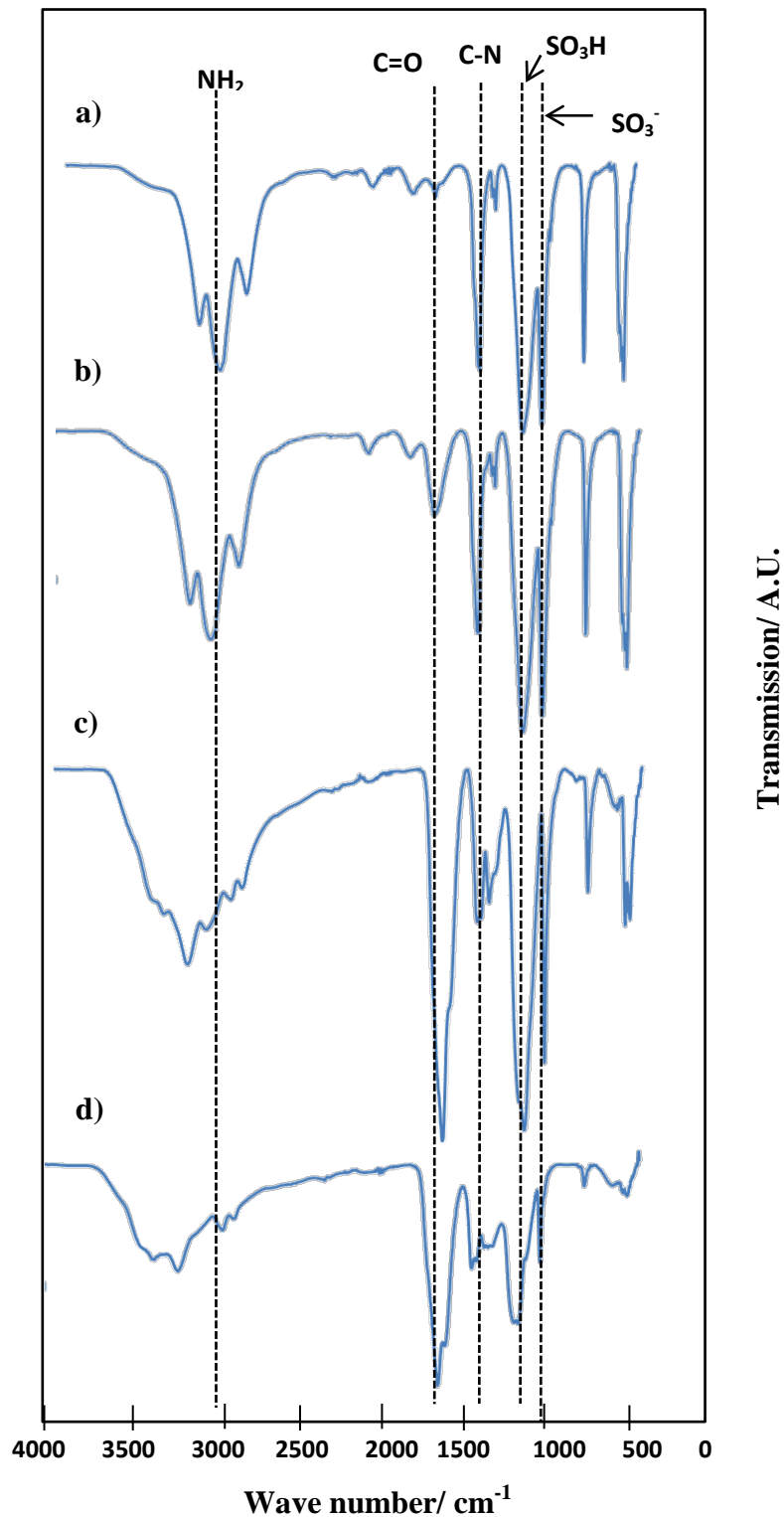


Figure 5: FTIR spectra of a) PAAm-4M MSA b) PAAm-5M MSA c) PAAm-6M MSA d) PAAm-7M MSA

3.2 FTIR of PAAm- Sulfonic acid Composite Solid Polymer Membranes.

Evidences for the interactions between the acids and the polymer were obtained from examination of the FTIR spectrums. From the FTIR spectra, the changes in the structures can be detected and subsequently can analyze the potential mechanism. The focus was given on the carbonyl group (C=O), amine group (NH₂) and (C-N) bond of the amide group because these functional groups provide an insight into the mechanism of bonding

between the PAAm and MSA molecules in the membranes synthesized.

Figure 5 shows the FTIR spectra of PAAm-MSA CSPE with the concentrations of MSA. The absence of OH peaks around $3000-3500\text{ cm}^{-1}$ in the FTIR study showed that there are no formation of hydrogen bonds between the water molecules and the polymer in the composites synthesized. The water molecules were dried out fully during the dehydration step. Thus, the water molecules did not involve in the proton transfer and conductivity.

The absorption bands at 1698 cm^{-1} for C=O [14] was clearly shifted to the lower wave numbers as the concentration of MSA increased from 4M to 7M. The membrane with 6M of MSA showed the greatest intensities of absorption. On the other hand, the intensity of vibration from NH_2 (3044 cm^{-1}) [17] decreases and moves to the higher wave numbers as the concentration of sulfonic acids increases. These observations indicated that the highest concentration of hydrogen bonds formed between the OH group of Methanesulfonic acid and carbonyl group (C=O) of polyacrylamide and not with the amide group (NH_2). Spectrum also suggested that Methanesulfonic acid did not protonate NH_2 to NH_3^+ in PAAm but interact with it by $\text{O-H}\cdots\text{O}=\text{C}$ to form hydrogen bonds (Figure 6). The mechanism of interaction between the acid molecules and the polymer in the composite membranes are different than in the GPEs of the PAAm-MSA of our previous study [14] where the NH_2 was protonated to NH_3^+ .

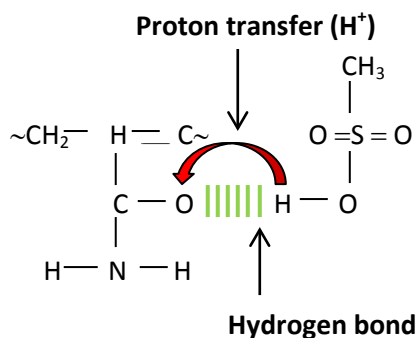


Figure 6: $\text{O-H}\cdots\text{O}=\text{C}$ interaction in the PAAm-MSA composite membrane

The protons are migrated along the hydrogen bonds formed between the OH group of acid and the C=O of the polymer in the PAAm framework. As the concentration of the acids increased, the intensity of the C=O peaks is decreased showed the reduction in the hydrogen bonds and consequently reduce the protons transfer and proton conductivities in the composites synthesized. The reduction of the hydrogen bonds are could be because of the reduction in the amount of the sulfonic acids caged in the PAAm frame work. This is further confirmed by the presences of the stretching vibration of sulfate groups, SO_3H (1155 cm^{-1}) [18,19] and SO_3^- (1037 cm^{-1}) [18,19] in the spectrums for the lower concentration of the acid but decreased in the intensities as the concentration of the acid increase. The vibration peak of 775 cm^{-1} is due to the C-S symmetric stretch in Methanesulfonic acid [18].

Thus, the FTIR results proved that the decreases in the proton conductivity as the concentration of acid increases is due to the reduction in the amount of acids caged in the polymer matrix which reduced the formation of

hydrogen bonds.

3.3 Thermal Analysis of the PAAm-MSA Composite Solid Polymer Electrolyte

The thermal stability of the PAAm Composite Solid Polymer Electrolyte with 5M MSA which gave the highest conductivity value was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Figure 7 shows that the composite degradation proceeds in the three stages. The first stage is due to the dehydration of the moisture present in the membrane, this continues up to 100°C, where the weight loss is about 2.24%. The second stage from 100°C to 286.67°C is due to the volatilization of the polymer and the weight loss of 18.52% was observed. During the next stage, the weight loss is further increased and reached a stable value of 33.84% at 500°C. After that, no major weight loss was observed up to 600°C. Differential scanning calorimetric analysis shows two peaks (Figure 8); the first one is due to the glass transition phenomenon and the other one to decomposition of the melt which took place at 286.67°C.

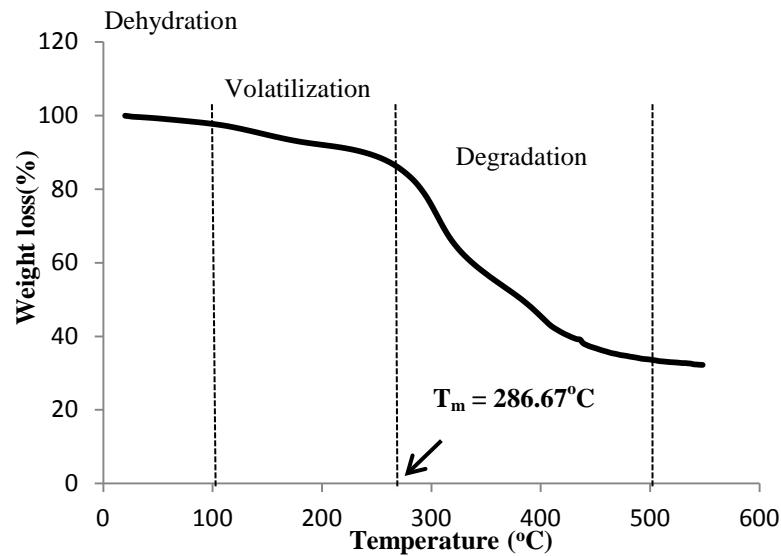


Figure 7: TGA Curve of PAAm-5M MSA CSPE

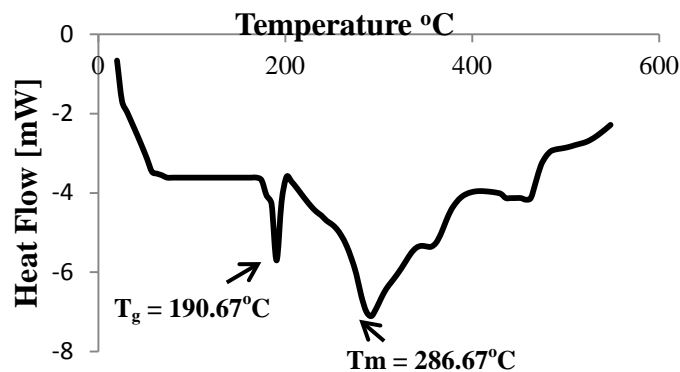


Figure 8: DSC Curve of PAAm-5M MSA CSPE

The values of T_g and T_m from the TGA and DSC curves of PAAm and PAAm-MSA acid are tabulated in Table 2.

Table 2: Tg and Tm values of the PAAm and PAAm-MSA CSPE synthesized

CPSEs	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$
PAAm [20,21]	161.4	237
PAAm- 5M MSA	190.67	286.67

The results demonstrated that the thermal stability of PAAm increased due to the added of MSA into the PAAm framework. The higher Tg and Tm of PAAm in these composite indicates that there are strong interaction between PAAm and sulfonic acid through hydrogen bond with 5M MSA which limited the chain movement of PAAm in the composite. Increased thermal stability of PAAm was also observed by other researchers in their studies [22,23,24].

3.4 Morphology of PAAm-5M MSA Composite Solid Polymer Electrolyte

The cross-sectional view of a PAAm-5M MSA composite membranes are shown in Figure 9 at different magnification. There was a scattered presence of granules with the sizes up to $\sim 20\mu\text{m}$ in the membranes. The microstructure shown in Fig 8 indicates that the resultant PAAm-5M MSA composite solid polymer electrolyte membrane is indeed a well interconnected, interpenetrating network capable of holding a large amount of MSA in the structure.

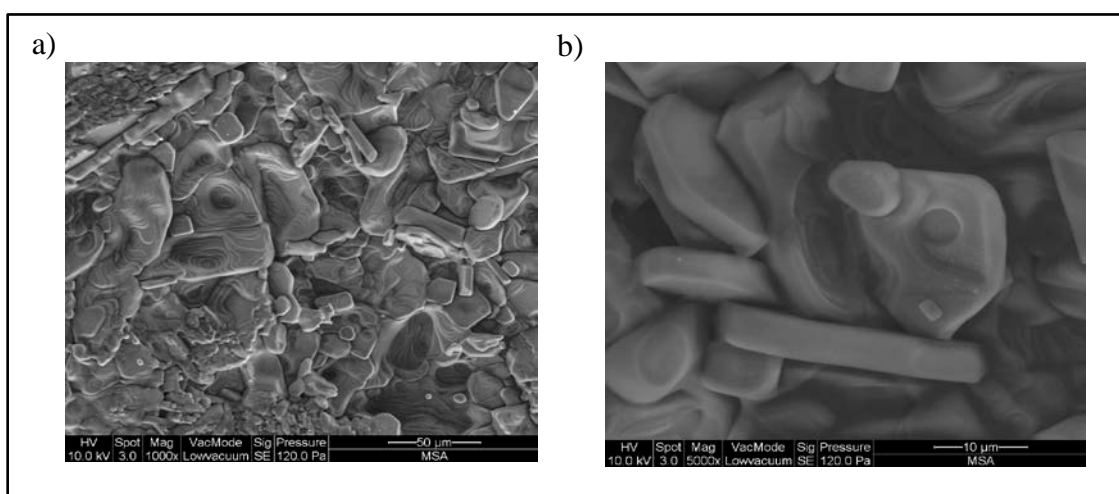


Figure 9: Cross sectional FESEM images of the PAAm-5M MSA membranes at (a) 1000x (b) 5000x of magnification

4. Conclusions

In summary, a new class of PAAm-MSA composite solid polymer electrolytes has been synthesized at room temperature by a simple and low-cost approach. An optimum proton conductivity of $1.17 \times 10^{-6} \text{Scm}^{-1}$ was observed at room temperature with the loading of 5M of MSA into the polymer matrix. The protons transport was facilitated by hydrogen bonds formed between O-H in the MSA acid and the functional group of C=O in PAAm. The membrane also exhibit excellent thermal stability. These profound advantages along with low-cost synthesis promise this new membrane and concept can be potentially used as composite solid polymer electrolytes in electrochemical devices.

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