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Conductivity studies on PMMA-Methanesulfonic acid based proton conducting polymer electrolytes

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Abstract: Solid polymer electrolyte films consisting of poly methyl methacrylate (PMMA) as host polymer, methanesulfonic acid (MSA) as inorganic acid (proton donar) are prepared by solution casting technique by using N,N-Dimethyl formamide as solvent. Complex nature of prepared proton conducting polymer electrolytes is confirmed by FTIR analysis. Pure PMMA contains a C-O stretching mode at 1227cm^{-1} which get shifted in the polymer-inorganic acid complexes. Ionic conductivity increases to 1.49x10^{-6} S/cm with increase in MSA concentration up to 19.12mol%. Further increase in MSA concentration, conductivity decreases due to ion aggregates. Dielectric spectra of PMMA-MSA membranes have also been studied.
Keywords: poly methyl methacrylate, methanesulfonic acid, N,N-Dimethyl formamide, FTIR.

1. Introduction and Experimental:

The potential utility of polymer electrolytes in high energy density batteries, energy conversion by fuel cells, chemical sensors etc has stimulated the synthesis of new polymer electrolytes, physical studies of their structure, charge transport and theoretical modeling of the charge transport processes [1]. Among the various solid polymer electrolytes, proton conducting polymer electrolytes received much attention due to their application in various electrochemical devices. Few reported proton conducting polymer electrolytes are complexes of strong inorganic acids (H_3PO_3, H_3PO_4, H_2SO_4, HCl) or ammonium salts (NH_4SCN, NH_4HSO_4, NH_4BF_4, NH_4I, NH_4NO_3) with commercially available electron donor polymers (PEO, PVP, PVA, PAA, PEI).

For the present work, the chosen host polymer is PMMA and MSA as the inorganic acid which donates protons. PMMA based polymer complexes found to exhibit the best characteristics due to their light weight, chemical resistance, good insulating properties and resistance to weathering corrosion. PMMA has an amorphous morphology and a polar functional group in its polymer chain that exhibits a high affinity for ions [2]. Jitender Paul Sharma et al reported that the conductivity is maximum for $PMMA_{15000}$ in their polymer gel electrolytes complexed with NH_4PF_6 [3]. Methanesulfonic acid is clear, colourless, strong organic acid but less corrosive and toxic.MSA has higher thermal stability and usually described as a “Green acid” [4]. Hence, current discussion deals with $PMMA_{15000}$-MSA based proton conducting polymer electrolyte membranes.

Polymethyl methacrylate (PMMA) (M_W=15,000) (HIMEDIA), Methanesulfonic acid (MSA) (Sd Fine – Chem) (LR) and N,N-Dimethyl Formamide (DMF) (Merck) were used to prepare proton conducting polymer electrolyte membrane by means of solution casting technique. The prepared samples are listed in Table1. FTIR spectra were recorded with computer interfaced JASCO FT/IR-4100 FTIR spectrometer at room temperature in 550-4000 cm^{-1} wave number range. Ionic conductivity of the samples was determined by IM6 Zahner elektrik work station, in the frequency range of 100mHz to 400KHz.

Table 1: Sample code and their composition of polymer electrolyte membrane

Sample	Composition of polymer electrolyte membrane
PS1	90.40mol% PMMA : 09.60mol% MSA
PS2	84.67mol% PMMA : 15.33mol% MSA
PS3	82.78mol% PMMA : 17.22mol% MSA
PS4	80.88mol% PMMA : 19.12mol% MSA
PS5	75.20mol% PMMA : 24.80mol% MSA

2. Result and Discussion:

2.1. FTIR Studies:

FTIR spectroscopy plays vital role in the investigation of polymer-inorganic salt/acid complexes. Due to different compositions and occurrence of complexation and interaction between various constituents, FTIR spectra of complexes vary. Transmittance mode of FTIR spectra for pure PMMA, pure MSA and their complexes are shown in Figure 1. The peak at 1227cm^{-1} of pure PMMA which corresponds to C-O stretching is shifted to 1211, 1215, 1219, 1220 and 1217cm^{-1} for the complexes PS1, PS2, PS3, PS4 and PS5 respectively. This shift is expected to be due to an interaction between C-O in PMMA and dissociated ions ($CH_3SO_3^-$, H^+) in MSA. The characteristic frequency of pure PMMA is observed at 1725cm^{-1} (C=O stretching) are not much shifted in the PMMA-MSA complexes. This suggests that very less interaction is between C=O in PMMA and MSA. The spectral features of MSA are found to be shifted appreciably in PMMA-MSA complexes. The above results confirm the complex formation.

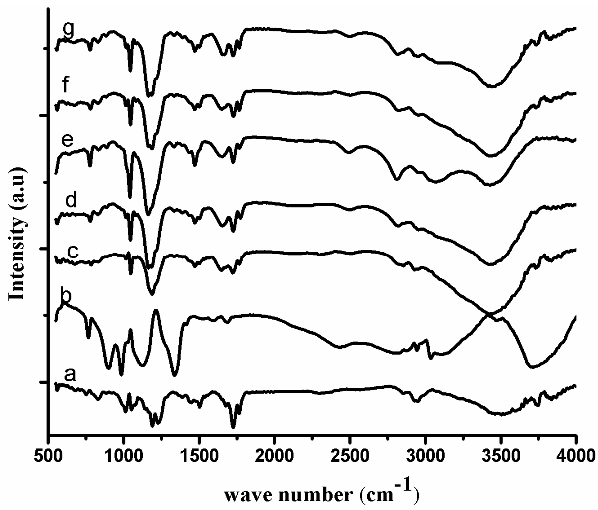

Figure 1: FTIR Spectra of a) Pure PMMA, b) Pure MSA, c) PS1 d) PS2 e) PS3 f) PS4 g) PS5

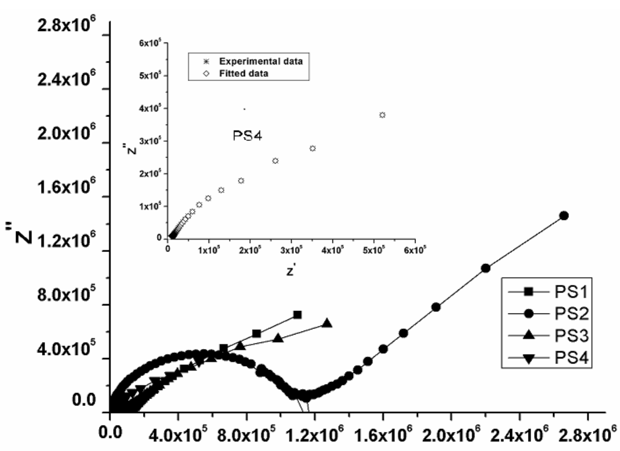

Figure 2(a): Impedance plot for PS1, PS2, PS3 and PS4 membranes

2.2. Impedance plot analysis:

A typical impedance plot (Z' Vs Z'') for PS1, PS2, PS3 and PS4 at ambient temperature are shown in figure 2(a). This Cole-Cole plot consists of one semicircular arc and a spike. Semicircle appearing at the higher frequency region corresponds to the bulk property of the electrolyte. The spike at lower frequency side is modeled to a capacitor corresponding to the double layer capacitance at the electrolyte – electrode interfaces. The bulk resistance (R_B) is obtained from the point of intersection on the real part of the Z-axis from which the value of σ can be calculated from the formula $\sigma = \frac{t}{AR_B}$ where t and A are the thickness and area of the membrane. The inset picture gives the experimental and fitted impedance plot for PS4 membrane. The calculated conductivity values of PS1, PS2, PS3, PS4 and PS5 at ambient temperature are 2.13 x 10^{-8}, 2.43 x 10^{-8}, 2.86 x 10^{-7}, 1.49 x 10^{-6} and 1.96 x 10^{-10}S/cm respectively.

2.3. Variation of ionic conductivity with MSA concentration:

Figure 2(b) shows the plot of ionic conductivity dependency on Methanesulfonic acid concentration at room temperature. The ionic conductivity increases with increase of acid concentration up to 19.12mol%. Increase in MSA content in polymer matrix, there is a possible increase of free ions. This may be the reason to get rise in conductivity until MSA content reaches 19.12mol%. The conductivity obtained at the acid concentration of 24.80mol% indicates that the ionic conductivity decreases. The possible decrease in ionic conductivity may be attributed to either an incomplete dissociation of salt or ion aggregates.

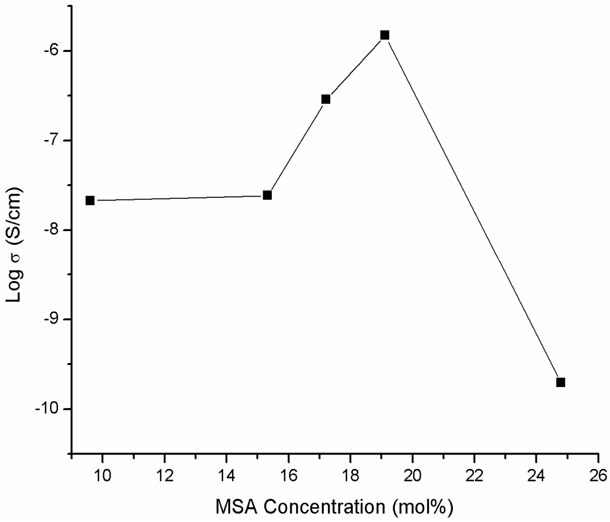

Figure 2(b): Variation of ionic conductivity with MSA

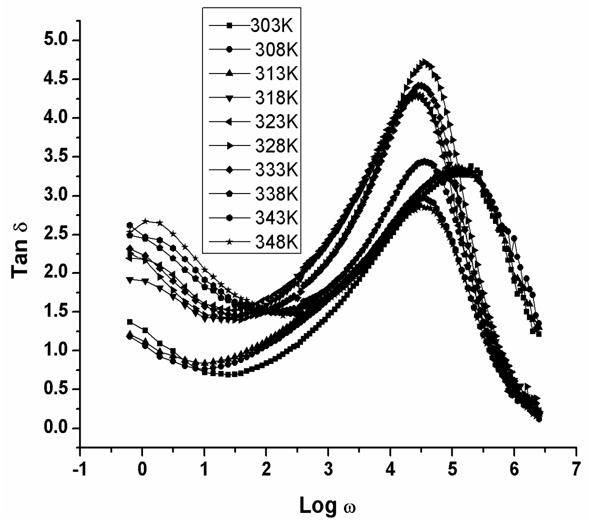

Figure 3: Logarithm of ω verses dissipation factor at various isotherms

2.4. Dielectric behavior:

The dissipation (loss) factor tanδ is given by the equation Tanδ=$\varepsilon''/\varepsilon'$. The plot between logω and Tanδ is shown in figure 3 for PS4 electrolyte at various temperatures. Two types of relaxations, one at low frequency region and the other at high frequency region are observed. The peak at the low frequency region corresponds to the relaxation occurs at electrode electrolyte interface. High frequency region peaks are attributed to conductivity relaxation.

2.5. Conclusion:

Proton conducting polymer electrolyte membrane, MSA complexed PMMA was prepared by simple solution casting technique. The maximum ionic conductivity of 1.49 x 10^{-6} at 303K has been obtained for the composition of 80.88mol% PMMA: 19.12mol% MSA polymer electrolyte system. Dielectric relaxation was observed for the prepared samples.

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