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Vibrational and Impedance analysis of polymer electrolyte based on pmma complexed with adipic acid

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Abstract

PMMA based proton conducting Polymer electrolytes with Pure PMMA and 80 PMMA: 20 $C_6H_{10}O_4$ have been prepared by Solution Casting Technique using DMF as solvent. FTIR studies reveal the complex formation between the salt and polymer matrix. Conductance spectra analysis reveals that the incorporation of salt Adipic acid to Pure PMMA dc conductivity value of Pure PMMA increases from 5.5758X10^{-7} Scm^{-1} to 1.5233X10^{-6} at ambient temperature. Admittance analysis is the double check for the conductivity obtained from conductance analysis. Magnitude Bode ploy shows the decline in the impedance with the addition of adipic acid to pure PMMA.

Keywords: Conductance, Bode plot, Admittance

1. Introduction

Solid polymer electrolytes have attracted the attention of scientists in the recent years, because of their impressive properties such as high ionic conductivity, flexibility and long life, which find applications in electrochemical devices. Solid polymer electrolytes have been extensively studied for their application as solid electrolyte in various electrochemical devices such as batteries, fuel cells, superconductors etc., In order to realize the technological of polymer electrolytes; they should have high ionic conductivity at ambient temperature with good mechanical stabilities. There are several organic dielectric materials that have been studied including poly (vinyl alcohol) (PVA), polyamide, poly (methyl methacrylate) (PMMA) and other. PMMA is chosen to be dielectric materials in organic thin film transistor (OTFT) and organic field effect transistor (OFET) because it has good insulation properties such as low dielectric constant and low dielectric loss over a wide range of frequency.

The present work aims at developing a polymer electrolyte based on PMMA: $C_6H_{10}O_4$ by Solution Casting Technique. Experimental techniques such as Fourier Transform Infrared Spectroscopy and Ac impedance Spectroscopy have been employed.

2. Experimental Procedure

Polymer electrolytes have been prepared using PMMA: $C_6H_{10}O_4$ in different molar ratios (100:0), (80:20) by solution casting technique with Dimethyl Formamide (DMF) as the solvent. PMMA is stirred in DMF at 24 hours and then $C_6H_{10}O_4$ is added and stirred at 55^0 C for 12 hours until the mixture become homogeneous viscous liquid. These solutions of different compositions have been poured into identical Petri dishes of 10 cm diameter and are dried in vacuum oven at room temperature for 24 hours. FTIR spectrum has been recorded in the range of 500-4000 cm^{-1} at room temperature using SHIMADZU Spectrophotometer. The impedance studies are made using a computer controlled HIOKI make LCZ meter in the frequency ranging from 42 Hz to 5 MHz at various temperatures ranging from 303K to 343K using stainless steel blocking electrodes.

3. Results and discussion

3.1 Fourier Transform Infrared analysis

FTIR has been used to study the complex formation between the polymer and the salt. FTIR is also used to study the interaction between cations, anions, solvents and polymers. This interaction is determined by the shift in the IR spectrum as well as the alteration in band shapes and the intensities of internal vibrational modes. Figure-1 represents the FTIR spectra of Pure PMMA and the polymer complex 80 PMMA: 20 Adipic acid. The vibrational frequencies observed in the FTIR spectra of Pure PMMA – $C_6H_{10}O_4$ polymer electrolytes are given in Table1.

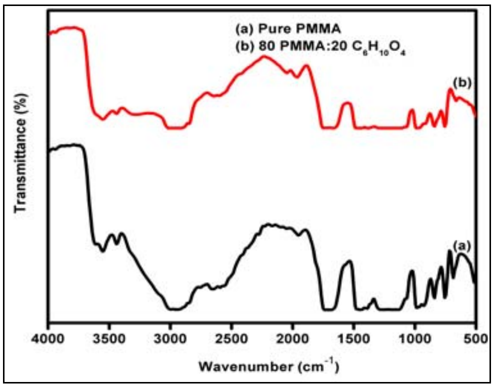

Fig 1: FTIR spectra

Table 1: Force Constant for Polymer Electrolytes

Assignment	**Vibrational Frequencies of PMMA: $C_6H_{10}O_4$ (cm^{-1})**		**Force constant (K)of PMMA: $C_6H_{10}O_4$ ($X10^5$ N/cm)**	
	100:0	**80:20**	**100:0**	**80:20**
O-C asym. Stretch	3441	3441	6.6156	6.6156
C = O stretch	1728	1751	1.2073	1.2399
CH_2 scissoring	1473	1481	7.6855	7.7658
C-O bend	925	918	4.7887	4.7092

The absorption peak at 3441 cm^{-1} attributed to O-CH_3 stretching of Pure PMMA has got no shift in the adipic acid added electrolytes. The vibrational peaks at 1728 cm^{-1}, 1473 cm^{-1} and 925 cm^{-1} are assigned to saturated polymeric ester C=O symmetric stretching [1], CH_2 scissoring and symmetrical stretching of C - O bend in the C-O-C linkage of Pure PMMA respectively [2]. These absorption peaks are shifted to 1751 cm^{-1}, 1481 cm^{-1} and 918 cm^{-1} respectively in 80 PMMA: 20 $C_6H_{10}O_4$ polymer electrolytes. The shifting and broadening of the absorption peak may occur due to the interaction ions with polymer. The above result confirms the complex formation between the polymer and the salt.

3.2 Force Constant

The force constant of molecules represents important physical constants. They are essential in the analysis of vibrational spectra. It is therefore significant to compile, arrange and store the force constants as many molecules as possible so that they can be readily utilized in the studies of molecular spectroscopy and molecular mechanics. Force constant (K) can be calculated by using the wave number (ν),

$$K = 4\pi^2 \nu^2 c^2 \mu \tag{1}$$

where c is the velocity of light and μ is the reduced mass. The use of reduced mass ensures that the center of mass of the molecule is not affected by the vibration. The force constants have been calculated for the observed peaks for both Pure PMMA and Adipic acid doped samples. The force constant values have been found to be changed for the salt doped samples. It indicates that there is interaction between salt and polymer.

3.3 Conductance spectra analysis

The conductivity of electrolytes (σ) depends on the charge carrier concentration (n) and mobility (μ). When the charge concentration is changed by doping the polymer with the salt then the conductivity is also expected to change. The conductivity of polymer electrolytes (σ) can be described by the basic relationship,

$$\sigma = nq\mu \tag{2}$$

Frequency dependent of the conductivity for all polymer electrolytes at 303K is portrayed in Figure-2.

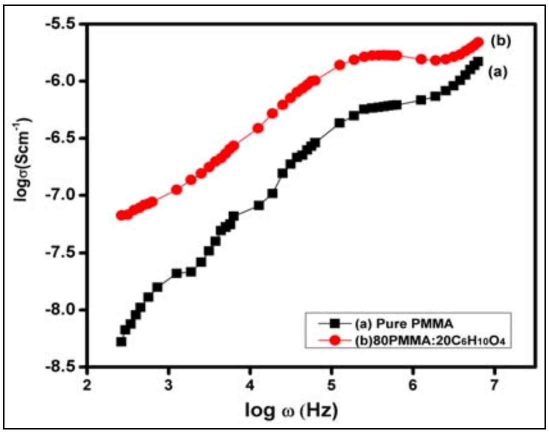

Fig 2: Conduction spectra

Table 2: Ionic conductivity of PMMA: C6H10O4 polymer electrolyte at 303K.

S. No.	**Composition (PMMA:C6H10O4) (mol %)**	**Ionic Conductivity (σ) (S/cm)**	
		Conductance Plot	**Admittance Plot**
1.	100:0	$5.5287X10^{-7}$	$5.8040X10^{-7}$
2.	80:20	$1.5233X10^{-6}$	$1.6732X10^{-6}$

The curve consists of three different regions namely low frequency dispersion region, plateau region and high frequency dispersion region. Low frequency dispersion region is due to space charge polarization at the blocking electrode followed by a frequency independent plateau region corresponding to dc conductivity of the polymer electrolyte and a dispersive region at higher frequencies is due to bulk relaxation phenomenon. The extrapolation of the plateau region to the log σ axis gives the value of the dc conductivity [3]. It has been noted that the incorporation of salt Adipic acid to Pure PMMA dc conductivity value of Pure PMMA increases from $5.5758X10^{-7}$ Scm^{-1} to $1.5233X10^{-6}$ at ambient temperature.

3.4 Admittance analysis

The admittance plot is a potent method to inspect the ion conduction mechanism. The complex admittance plot is shown by the relation,

$$Y^* = Y' + Y'' \tag{3}$$

Where Y′ and Y″ is the real and imaginary part of the admittance respectively.

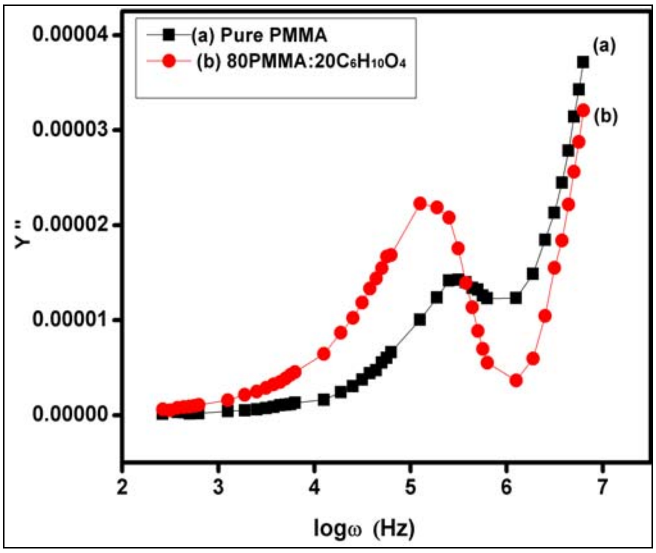

Fig 3: Imaginary part of Admittance spectra

Spectroscopic plot of imaginary part of the admittance of all samples is depicted in Fig. 3. The admittance value increases with increase in frequency and reaches maximum and then decreases. The existence of peak reveals the relaxation mechanisms [4]. The presence of the peak in the spectroscopic plot of Y" indicates that there is series combination of bulk resistance and electrode capacitor with peak maximum at $1/2R_b$. The bulk resistance (R_b) obtained from peak maximum has been used to calculate the ionic conductivity by the relation

$$\sigma = \ell / R_b A \tag{4}$$

where l is the thickness of the polymer electrolyte and A is the surface area of the electrolyte. From the table 1, it has been observed that the ionic conductivity of all electrolytes calculated using admittance analysis is concord with that obtained from conductance spectra.

3.5 Magnitude Bode Plot Analysis

The complex impedance is expressed as

$$Z = |Z| e^{j\theta} \tag{5}$$

where $|Z|$ and θ are the absolute magnitude and the phase angle of impedance.

$$|Z| = (Z'^2 + Z''^2)^{1/2} \tag{6}$$

$$\theta = \text{arc tg}\left(\frac{Z''}{Z'}\right) \tag{7}$$

Where Z' and Z'' are the real and imaginary parts of complex impedance.

$$Z = Z' - jZ'' \tag{8}$$

Angular frequency dependence of the modulus impedance $|Z|$ is depicted in Figure 4. The modulus impedance coincides in the high frequency region for all electrolytes. The Ohmic resistance dominates the impedance at the highest frequencies and it can be read from the high frequency horizontal plateau region. In the intermediate frequency region the modulus Z decreases with increase in frequency. It is due to reactive component (capacitative) component to the current which is dominating over the Ohmic current. The reactive component of the current is frequency dependent while the active component of the current is independent of frequency.

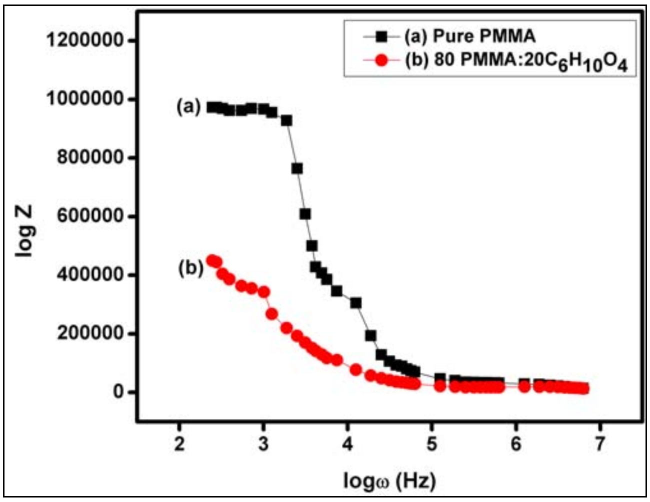

Fig 4: Magnitude Bode Plot

3.6 Phase Bode Plot analysis

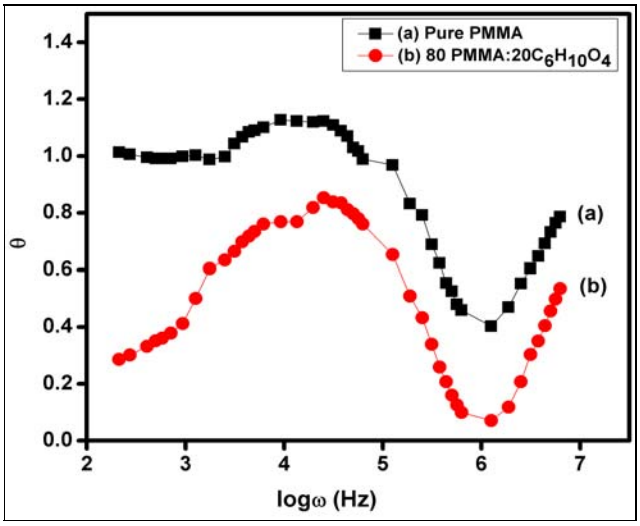

Fig 5: Phase Bode Plot

Fig 5 shows the Bode plot format of the phase angle (ɵ) as a function of frequency of pure PMMA and 80 PMMA: 20 $C_6H_{10}O_4$. In the low frequency region, the phase angle is nearly zero. It indicates the resistor like behavior. In the intermediate frequencies, the phase angle increases as the frequency increases and reaches maximum. The frequency dependent phase shift is due to capacitative reactance of the current which depends upon the frequency. The double layer capacitance can be calculated from the peak maximum.

4. Conclusion

PMMA based proton conducting Polymer electrolytes with Pure PMMA and 80 PMMA: 20 $C_6H_{10}O_4$ have been prepared by Solution Casting Technique using DMF as solvent.

- FTIR studies reveal the complex formation between the salt and polymer matrix.
- The highest ionic conductivity has been found to be $1.52X10^{-6}$ Scm^{-1} for 80 PMMA: 20 $C_6H_{10}O_4$ polymer electrolyte from the Conductance plot and also confirmed from Admittance spectra.
- Angular frequency dependence of the modulus impedance shows the high frequency horizontal plateau region.
- The frequency dependent phase shift is due to capacitative reactance of the current.

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