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Magnitude Bode Plot Analysis of Solid Polymer Electrolyte PMMA Complexed with Adipic Acid

K. P. Radha*, P. Mahalakshmi and S.Chitra

Department of Physics, S.F.R. College for Women, Sivakasi, Tamilnadu, India

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ABSTRACT

In the present work, proton conducting solid polymer electrolyte have been prepared using PMMA and adipic acid ($C_6H_{10}O_4$) by Solution Casting Technique. From the Magnitude Bode Plot, it has been observed that the Ohmic resistance dominates the impedance at the highest frequencies and it can be read from the high frequency horizontal plateau region. Argand plots of both pure PMMA and adipic acid added electrolyte are incomplete half semicircle suggesting the Non - Debye nature of the polymer electrolytes. At higher frequencies due to the periodic reversal of the electric field there is no excess ion diffusion in the field direction. The presence of long tail in the modulus plot may be due to the large capacitance associated with the electrodes.

Key - words: Argand, Dielectric, Modulus plots

INTRODUCTION

Polymer electrolytes combine ionic conductivity in the solid state with mechanical flexibility, making them ideal replacement for liquid electrolytes in electrochemical cells such as Fuel cell, electro chromic displays, sensors etc., because of their ability to form good interfaces with solid electrodes. PMMA is a polymer which forms complexes with inorganic salts such as NH_4PF_6 LiCF3SO3, $LiNO_3$ etc.[1]. It has excellent chemical and physical properties which has made it of great interest in proton conducting solid polymer electrolytes. In the present work, we report the effect of adipic acid on the characterization of conventional proton conducting solid polymer electrolytes based on PMMA in terms of dielectric behavior, ionic conductivity and the interactions that had occurred between them.

MATERIALS AND METHODS

2.1 Sample Preparation

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 55^0C 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. Free standing nature of the electrolyte has obtained.

2.2 Conductivity Measurements

AC conductivity measurements have been carried out on PMMA: $C_6H_{10}O_4$ systems of uniform thickness having an area of 1 cm^2. Polymer electrolytes have been sand witched between two stainless steel (SS) electrodes applying a potential of 1V from 42 Hz to 1 MHz using HIOKI make LCZ meter (model 3532) interfaced to a computer. The conductivity have been calculated from complex impedance plots of measured impedance (Z) and phase angle (θ). The temperature of the cell has been controlled using a thermostat and electrical measurements of the polymer electrolytes have been carried out in the temperature range 303K – 343K.

RESULTS AND DISCUSSION

3.1 Magnitude Bode Plot

The complex impedance is expressed as

$$Z^* = |Z| e^{j\theta}$$

where $|Z|$ and θ are the absolute magnitude and the phase angle of impedance [2]. Frequency and temperature dependence of the modulus impedance $|Z|$ is depicted in Figure 1. 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) 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. The impedance decreases with rise in temperature in the low frequency region indicating the temperature dependence of the ionic conductivity.

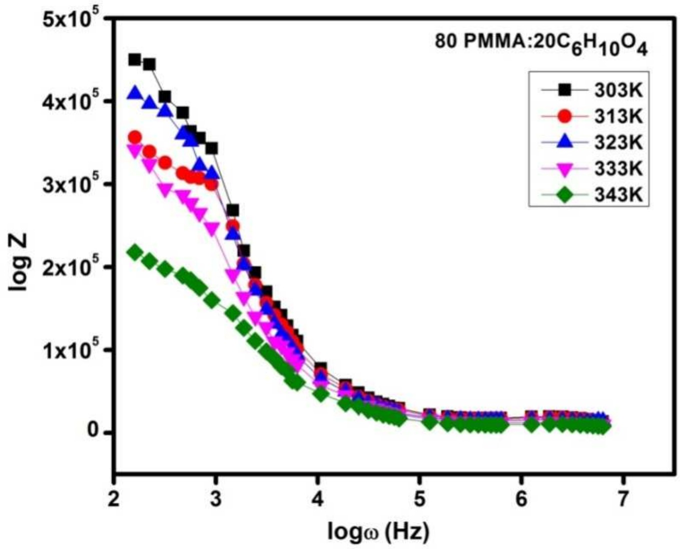

Fig. 1 Magnitude Bode plot

3.2 ARGAND PLOT ANALYSIS

The nature of relaxation processes present in the polymer electrolytes can be demonstrated by the study of Argand plot. Fig 2 shows the temperature dependence of Argand plots of pure PMMA and 80PMMA:20 $C_6H_{10}O_4$ polymer electrolytes at ambient temperature. From the fig, it is obvious that the curves of both Argand plots are incomplete half semicircle which cannot be explained by Debye model which has single relaxation time. Our Argand plots show deformed arcs for both undoped and doped PMMA polymer electrolytes with their centers positioned below the horizontal axis. This position, in principle corresponds to the electric relaxation in polymeric materials with both the relaxation time and activation energy distributed and intercorrelated according to the author Calleja [3]. The author Matveeva reported that the radius of the arc of the Argand plot is dependent on the electrical conductivity of the electrolytes that is the larger arc means lower electrical conductivity [4]. In our case, the radius of arc decreases for adipic acid added polymer electrolyte which means that the ionic conductivity of the electrolyte increases for $80PMMA:20C_6H_{10}O_4$ polymer electrolyte. This can be ascribed to the increase of ionic conductivity [5]. The effect of adipic acid on pure PMMA results in the enhancement of ionic conductivity from 5.5287 X 10^{-7} Scm^{-1} to 1.5233 X 10^{-6} Scm^{-1} at ambient temperature.

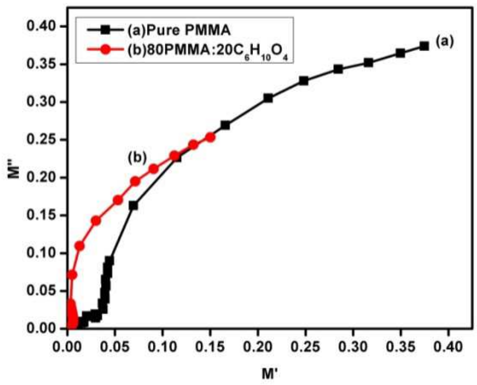

Fig 2 Argand Plot

3.3 Dielectric Spectra Analysis

The dielectric behavior of the polymer electrolyte system is described by the relation,

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

where ε′ and ε″ are the real and imaginary part of the dielectric constant of the material respectively.

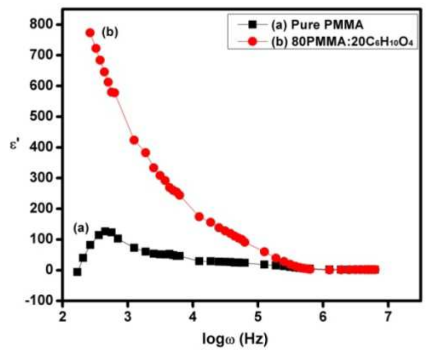

Fig. 3 Frequency Vs real part of dielectric permittivity plot

Figure 3 and 4 stands for the frequency dependence of ε′ (ω) and ε″ (ω) for Pure PMMA and 80 PMMA : 20 $C_6H_{10}O_4$ polymer electrolytes at 303K respectively. It has been noted that the values of ε′ (ω) are high at low frequency. The low frequency dispersion region is due to the accumulation of charge carrier near the electrode. At higher frequencies due to the periodic reversal of the electric field there is no excess ion diffusion in the field direction. The polarization due to the charge accumulation decreases with increase in frequency leading to decrease in the values of ε′ and ε″. The large value of ε″ (ω) in the low frequency region is attributed to the motion of free charge carriers within the material.

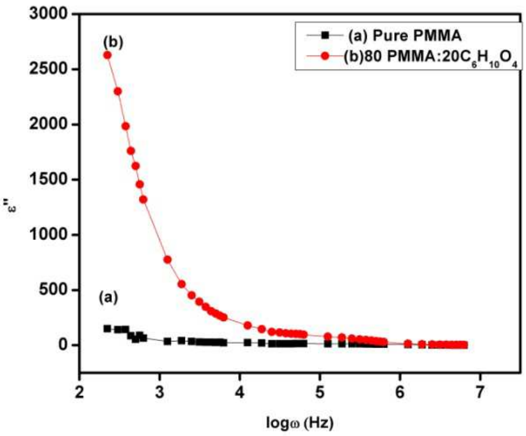

Fig.4 Frequency Vs imaginary part of dielectric permittivity plot

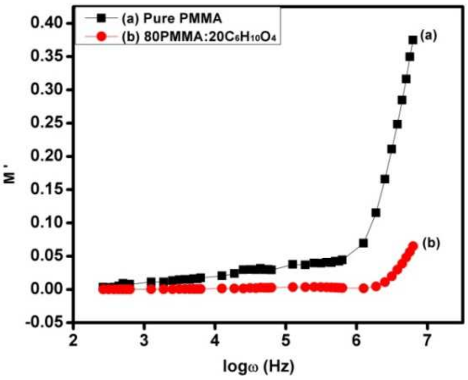

Fig.5 Real part of Modulus spectra

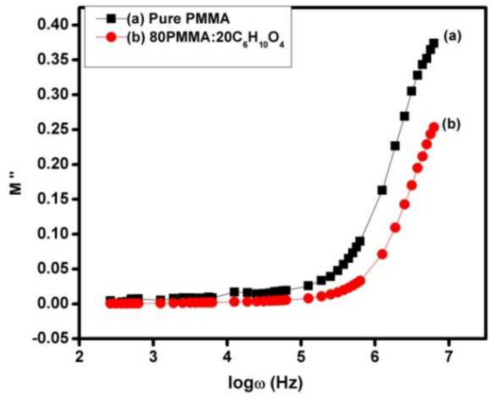

Fig.6 Imaginary part of Modulus spectra

3.4 Modulus Spectra Analysis

The electric modulus can be represented by the following equation,

$$\mathbf{M^*} = M' - \mathbf{jM''}$$

where M′ and M″ are real and imaginary part of the complex electric modulus. The frequency dependence of M′ and M″ for all polymer electrolytes is shown in the figure 5 and 6 respectively. It is observed that, at higher frequencies the intensity decreases with rising concentration of salt adipic acid. At low frequencies the value of M″ is in the vicinity of zero indicating that the effect of electrode polarization is negligible. The long tail in the both plots may be due to the large capacitance associated with the electrodes [6].

CONCLUSION

PMMA based Proton conducting Solid 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.

❖ Magnitude Bode plot analysis reveals that the impedance decreases with rise in temperature in the low frequency region. It indicates the temperature dependence of the ionic conductivity.

❖ Our Argand plots show deformed arcs for both salt adipic acid undoped and doped PMMA polymer electrolytes with their centers positioned below the horizontal axis. It suggests non Debye nature of the solid polymer electrolytes.

❖ The large value of ε″ (ω) in the dielectric spectra is attributed to the motion of free charge carriers within the material.

❖ At low frequencies the value of M″ is in the vicinity of zero indicating that the effect of electrode polarization is negligible.

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