International Journal of Advanced Scientific Research
ISSN: 2456-0421
www.newresearchjournal.com/scientific
Volume 1; Issue 1; April 2016; Page No. 21-24

Dielectric and ionic conductivity analysis of solid polymer electrolyte based on PMMA

Mahalakshmi P, Chitra S, * Dr. Radha KP

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

Abstract

An attempt has been made to prepare a new proton conducting solid polymer electrolyte based on PMMA doped with adipic acid ($C_6H_{10}O_4$) by Solution Casting Technique. The complex admittance plot consists of low frequency arc and high frequency spike. Arrhenius plot analysis shows that the addition of adipic acid to PMMA enhances the ionic conductivity of Pure PMMA solid polymer electrolyte from $5.8040X10^{-7}Scm^{-1}$ to $1.6732X10^{-6}$ Scm^{-1} at ambient temperature. The curves in the Argand plot at different temperatures are incomplete half semicircle suggesting Non - Debye nature of the electrolytes. The long tail in the low frequency range of M' spectra indicate the capacitive nature of the system.

Keywords: Arrhenius, Argand, Bode plot, Admittance

1. Introduction

Solid Electro Chemical Devices based on Solid Polymer Electrolytes has attracted great scientific interests over the conventional liquid electrolyte due to the problems of leakage. Solid Polymer electrolytes have various advantages such as fast charge transfer at electrode interface, flexibility, electro chemical stability, light weighted mechanical strength and good processability. Unfortunately the low conductivity of the solid polymer electrolytes at room temperature limits their practical applications. Thus various efforts have been done to improve the proton conductivity of solid polymer electrolytes. One of the most successful approaches to enhance ionic conductivity is to add salts. Many proton conducting polymer electrolytes such as PVP: NH_4SCN, PEO; NH_4ClO_4, Chitosen: NH_4NO_3 etc are available in the literature, and they have exhibited excellent proton conductivity. It reveals that ammonium salts are very good proton donors. In this continuation, an attempt has been made to prepare and characterize a new proton conducting solid polymer electrolyte based on PMMA doped with adipic acid ($C_6H_{10}O_4$).

2. Experimental Procedure

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 55^0 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. 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 (ɵ). 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.

3. Results and discussion

3.1 Admittance analysis

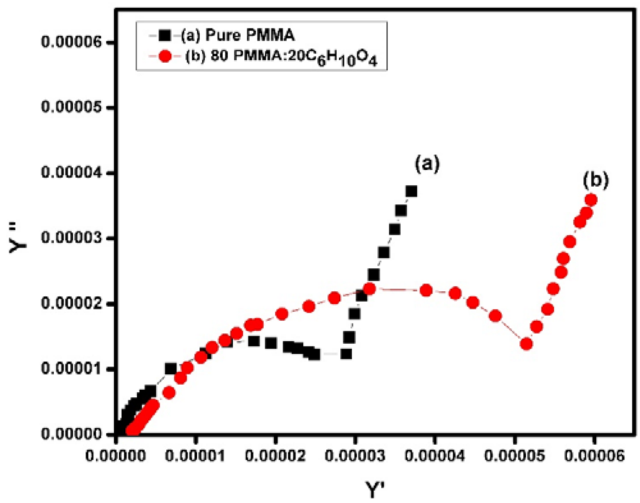

Fig 1: Complex Admittance plot

The complex admittance plot is a powerful method to investigate the ion conduction mechanism. The complex admittance Y^* is given by the relation

$$Y^* = 1/Z^* = Y' + jY'' \quad (1)$$

Where Y and Y is the real and imaginary part of admittance respectively. Fig 1 [a, b]. Shows Y vs Y of all samples at 303K. The plot shows a low frequency arc and high frequency spike. The spike represents the bulk response. The bulk capacitance (C_b) can be calculated at any point along this spike using the relation

$$C_b = \frac{Y''}{\omega} \quad (2)$$

Low frequency arc representing the series combination of the bulk resistance (R_b) and electrode capacitance C_e as shown in the equivalent circuit 1.

Equivalent Circuit 1

The intercept of the low frequency arc on the real axis is $1/R_b$. The value of $1/R_b$ of all samples have been obtained from curve fitting method. Then the conductivity of all samples have been calculated using the relation

$$\sigma = \ell / R_b A \quad (3)$$

Where 'ℓ' is the thickness of the polymer electrolyte and A is the surface area of the electrolyte. The calculated values are presented in table – 1. The addition of the salt adipic acid to PMMA enhances the amorphous phases of polymer matrix which in turn increases the ionic conductivity. Similar results have been reported by the author Hema [1].

Table 1: Ionic conductivity PMMA: C6H1004 polymer electrolytes at 303K.

S. No.	Composition (PMMA: C6H1004)	Ionic conductivity (S/cm)
1.	100:0	$5.8040X10^{-7}$
2.	80:20	$1.6732X10^{-6}$

3.2 Temperature Dependence of Ionic Conductivity

The temperature dependence of conductivity for (Pure PMMA) and (80 PMMA: 20 $C_6H_{10}O_4$) polymer electrolytes over a temperature range 303-343K is shown in figure 2.

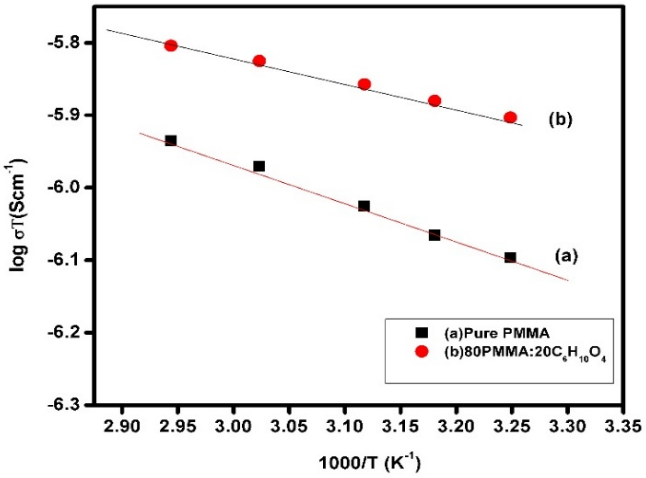

Fig 2: Arrhenius plot

The plot shows that the conductivity increases with increase of temperature. The calculated regression values for all the electrolytes are close to unity which suggests Arrhenius type, thermally activated process. This indicates that the plots obey Arrhenius law,

$$\sigma T = \sigma_0 \exp(-E_a / kT) \quad (4)$$

Where σ_0 is the pre-exponential factor and E_a is the activation energy for conduction. The nature of cation transport is quite similar to that occurring in ionic crystal, where ions jump in to neighboring vacant sites and hence, increase conductivity to higher value it is also understood that the increase in conductivity with temperature can be linked to the decrease in viscosity and hence increased chain flexibility [2]. The activation energy E_a, evaluated from the slope of the plots, regression and standard value of Pure PMMA and 80 PMMA: 20 $C_6H_{10}O_4$ electrolytes have been presented in the table 3. The incorporation of 20mol% adipic acid to Pure PMMA lowers the activation energy of Pure PMMA from 0.1438eV to 0.1275eV. It may be due to decrease in the energy barrier to the proton transport in the polymer matrix [3].

Table 3: Activation energy, Regression and Standard value of polymer electrolytes

Composition (mol %)	Activation energy, E_a (eV)	Regression	Standard value
Pure PMMA	0.1438	0.96825	0.03219
80PMMA: 20 $C_6H_{10}O_4$	0.1275	0.99421	0.01565

3.3 Argand plot analysis

The nature of relaxation processes present in the polymer electrolytes can be demonstrated by the study of Argand plot at different temperatures. Figure 3 shows the temperature dependence of Argand plot of 80PMMA:20$C_6H_{10}O_4$ polymer electrolyte. From the fig, it is obvious that the curves of argand plot at different temperatures are incomplete half semicircle which cannot be explained by Debye model (i.e single relaxation time). The author Kwan has reported many reasons for the existence of relaxation times distributed in solids such as hopping, space charge polarization and inhomogenetics [4].

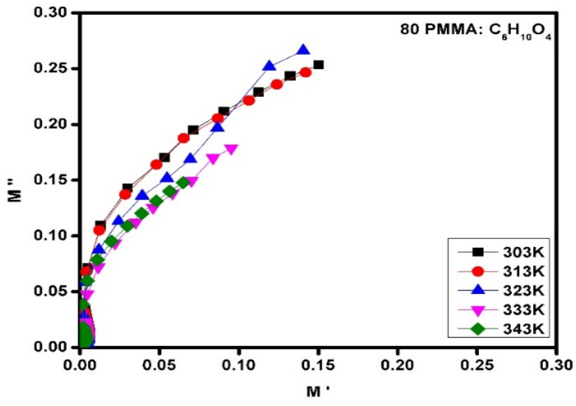

Fig 3: Argand plot

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 [5]. In our case, the radius of arc decreases with rise in temperature which means that the ionic conductivity of the electrolytes increases with temperature. This can be ascribed to the increase of ionic conductivity leading to increase in ionic mobility with temperature [6].

3.4 Modulus spectra analysis

The real part (M') and imaginary part (M") of electrical modulus have been calculated using the following equations:

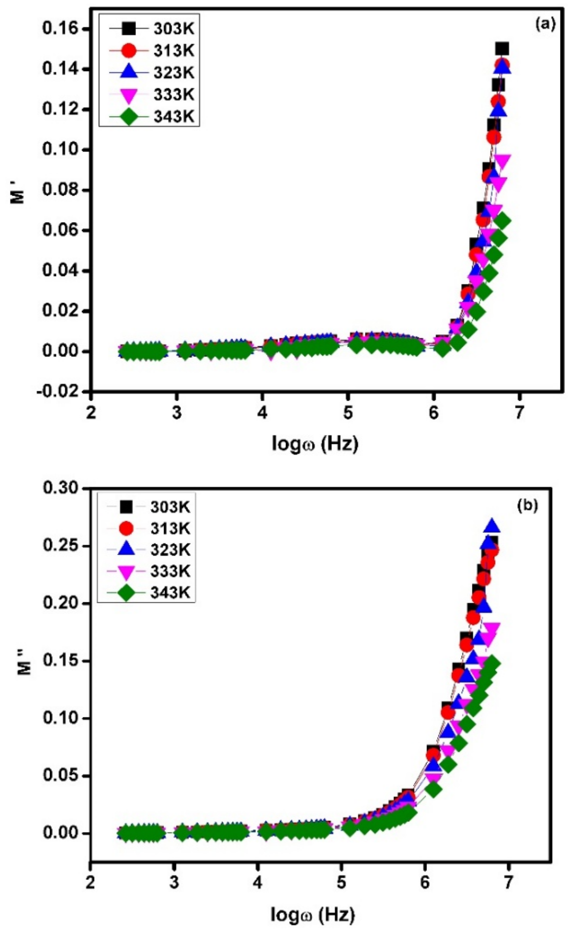

Fig 4: (a) Real and (b) Imaginary part of Modulus spectra

$$M' = \frac{\varepsilon'}{\varepsilon' + \varepsilon''} \quad (5)$$

$$M'' = \frac{\varepsilon'}{\varepsilon' + \varepsilon''} \quad (6)$$

Figure 4 (a, b) depicts the frequency dependence of M′ and M″ of 80 PMMA: 20 C6H10O4 polymer electrolytes at different temperatures respectively. The presence of long tail at low frequency region reveals the presence of large capacitance related with the electrodes. The modulus peak maximum shifts to higher frequencies and the peak maximum value decreases with increase of temperature recommending the presence of more than one type of relaxation mechanisms [7]. It is in concord with the Argand plot analysis.

3.5 Phase Bode plot analysis

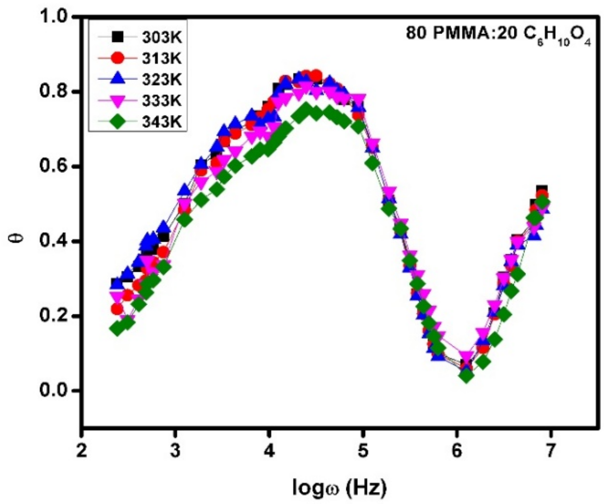

Fig 5: Phase Bode plot

Fig 5 shows the frequency dependence of the phase angle θ as a function of frequency of 80 PMMA: 20 C6H10O4 polymer electrolytes. In the low frequency region, the phase angle is nearly zero. It indicates the resistor like behavior. In the intermediate frequencies, 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

Proton conducting Solid Polymer electrolytes based on PMMA have been prepared by solution casting technique.

- The maximum ionic conductivity has found to be $1.6732 X 10^{-6}$ Scm^{-1} at 303K for Adipic acid doped Polymer electrolytes.
- The prepared polymer electrolytes obey Arrhenius equation.
- Argand plot analysis shows the non-Debye nature of the polymer electrolyte.
- The long tail in the low frequency range of M' spectra indicate the capacitive nature of the system.

- The M'' spectra shift to higher frequency for the sample with the highest conductivity due to the increase of mobile charge carriers.

5. References

1. Hema M, Selvsekarapandian S, Nithya H, Sakunthala A, Arunkumar D. Structural and Ionic conductivity studies on proton conducting polymer electrolyte based on polyvinyl alcohol Ionics. 2009; 15(4):487-491.
2. Selvsekarapandian S, Baskaran R, Hema M, Complex AC. impedance. Transference number and vibrational spectroscopy studies of proton conducting PVAc-NH_4SCN polymer electrolytes, Physica B, Condensed matter. 2005; 357:412-419.
3. Druger SD, Nitzan A, Ratner MA. Dynamic bond percolation theory: a microscopic model for diffusion in dynamically disordered system. I. Definition and one-dimensional case J Chem Phys. 1983; 79:3133-3142.
4. Kwan KC, Dielectric Phenomena in Solids, Elsevier, New York. 2004.
5. Matveeva ES. Introduction of Conducing Polymers Synth. Met. 1996; 79:127.
6. Aziz SB, Abidin ZHZ, Arof AK, Influence Of Silver Ion Reduction On Electrical Modulus Parameters Of Solid Polymer Electrolyte Based On Chitosan Silver Triflate Electrolyte Membrane, Express Polymer Letters. 2010; 4(5):300-3105.
7. Radha KP, Selvasekarapandian S, Karthikeyan S, Hema M, Sanjeeviraja C. Synthesis and impedance analysis of proton-conducting polymer electrolyte PVA:NH_4F, Ionics. 2013; 19(10):1437-1447.