

# Investigation on ionic conductivity of PVA-PEG-Mg(CH<sub>3</sub>COO)<sub>2</sub> Polymer electrolytes

D.Ravindran\*, P.Vickraman

*Department of Physics, Thiagarajar college of Engineering, Madurai, India*

*Department of Physics, Gandhigram Rural University, Gandhigram, Dindigul, India*

## Abstract

*Poly vinyl alcohol(PVA) and Poly ethylene glycol(PEG) blend based polymer electrolytes has been prepared using Mg(CH<sub>3</sub>COO)<sub>2</sub> as salt by varying the PEG: Mg(CH<sub>3</sub>COO)<sub>2</sub> ratio. The ionic conductivity of the prepared films was studied through XRD and AC impedance techniques. The temperature dependence conductivity shows Arrhenius behaviour. The maximum conductivity of 3.185X10<sup>-5</sup> was observed for the film with composition PVA-PEG- Mg(CH<sub>3</sub>COO)<sub>2</sub>: ( 40-50-10)*

## 1. Introduction

The research and development of polymer electrolyte based batteries with high specific energy, good reliability and safety has been an active research area for the past three decades [1-3]. Advances in micro electronic industry especially mobile phones, portable computers have created a demand for new and improved power sources. The world wide efforts are directed towards the development of advanced battery technologies based on lithium. The rechargeable lithium ion battery has been one of the best choices in view of the specific capacity and cyclic stability [4]. But these batteries are relatively expensive and suffer from safety limitations. Hence new rechargeable battery systems are required which can be made of cheap and environmental friendly materials.

Magnesium based rechargeable battery system has attracted attention due to its performance capabilities, which are expected to be close to those of lithium based rechargeable batteries[5]. Studies on solid state rechargeable magnesium batteries are important due to the following reasons. i) Magnesium is more stable than lithium; it can be handled safely in oxygen and humid atmospheres unlike lithium which requires high purity argon or helium atmosphere. Hence safety

problem associated with magnesium are minimal ii) the ionic radii of Li<sup>+</sup> and Mg<sup>2+</sup> are comparable in magnitude [6].iii) natural resources of magnesium are plentiful and thus it is cheaper than lithium. However investigation related to solid state rechargeable magnesium batteries are scarce in literature except a few reports [7, 8].

In the context of solid state rechargeable magnesium batteries, investigations on Mg<sup>2+</sup> ion conducting SPE are important. Poly (vinyl alcohol) (PVA) is a polymer which has been investigated by many researchers for its application as electric double layer capacitors, electro chromic windows, fuel cells etc., because of its excellent mechanical strength, electrochemical stability, high tensile strength and abrasion resistance[9]. It contains carbon chain backbone with hydroxyl groups attached to methane carbons. These OH groups can be a source of hydrogen bonding hence the assistance in the formation of polymer blends [10]. Most of the studies have been carried out on high molecular weight polymers. However not much attention has been paid to lower molecular weight polymers. Poly ethylene glycol (PEG) has the same monomeric unit as PEO, but has an end hydroxyl group, with the chemical formula H(-CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>n</sub>-OH. In the present communication, ionic conductivity of PVA-PEG blend based polymer electrolytes are investigated by incorporating Mg(CH<sub>3</sub>COO)<sub>2</sub> as salt through xrd and ac impedance analysis.

## 2. Experimental

Poly (vinyl alcohol) (PVA) with an average molecular weight of 1,25,000 and Poly ethylene glycol (PEG) with average molecular weight of 200 were purchased from CDH, India. Magnesium acetate (CDH, India) was dried at 40C for 24 h before using it. Polymer electrolytes were prepared using the solution casting technique. Appropriate quantity of PVA was dissolved in high purity distilled water with rigorous stirring for about 4-5 h. the required quantity of salt was dissolved in minimum quantity of distilled water and these two solutions were mixed and stirred gently. To this pre determined value of PEG was added and the solutions were continuously stirred for about 10-12 h

and the resulting homogeneous solution were poured on cleaned Petri dish and allowed to evaporate at room temperature under vacuum. The dried samples were transferred in to a desiccator for further drying before test. The prepared samples were free standing and thickness of the samples varied from 80-110  $\mu\text{m}$ .

The Polymer electrolyte films were subjected to X-ray diffraction studies to investigate the nature of crystallinity using JEOL, JDZ 8030 X-ray diffractometer at temperature 25°C. The ionic conductivity measurements were carried out with the help of stainless steel blocking electrodes by using a computer controlled micro Auto lab type III Potentiostat/Galvanostat of frequency range 50 Hz-100 KHz.

### 3. Results and discussion

#### 3.1 X-ray diffraction studies

The X-ray diffraction analysis is a useful tool to determine the structure and crystallization of the polymer matrices. In order to investigate the effect of blending in the PVA-PEG-Mg(CH<sub>3</sub>COO)<sub>2</sub> system XRD analysis has been performed and their respective diffraction patterns of pure PVA, PEG, Mg(CH<sub>3</sub>COO)<sub>2</sub> and the film with composition (PVA-PEG-Mg(CH<sub>3</sub>COO)<sub>2</sub> : 40-50-10) are shown in Fig1(a-d). The diffraction pattern of PVA show a sharp peak at  $2\theta = 20^\circ$ . The peaks pertaining to PEG ( $2\theta = 19.2^\circ$  &  $23.4^\circ$ ) are shown in Fig1.b. The peaks corresponding to Mg(CH<sub>3</sub>COO)<sub>2</sub> at  $2\theta = 20.8, 27.7, 32.3$  disappear in the electrolyte film indicating that the salt is completely solvated by the host polymer. The suppression the peak corresponding to PVA show that the decrease in the crystallinity of the complex. This feature is needed as the ion conduction takes place in the amorphous region.

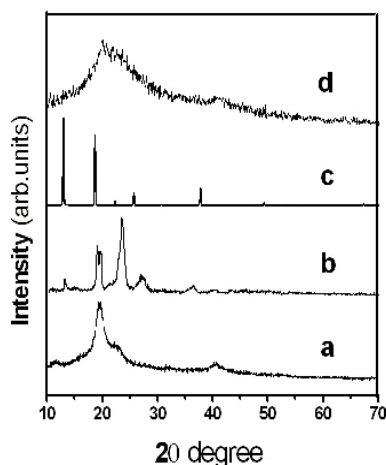


Fig 1. XRD patterns of a) pure PVA b) PEG c) Mg(CH<sub>3</sub>COO)<sub>2</sub> d) film with composition PVA-PEG- Mg(CH<sub>3</sub>COO)<sub>2</sub> : (40-50-10)

#### 3.2 AC impedance studies

Impedance spectroscopy is employed to establish the conduction mechanism observing the participation of the polymeric chain mobility and carrier generation processes. The samples were cut as per the required dimension and sandwiched between two stainless electrodes specially designed that exert a small pressure on the sample to ensure good contact. The impedance measurements were carried out using CH instruments in the frequency range 50 Hz to 100 KHz. The signal level was kept at 5mV. The conductivities of the polymer complexes were calculated from the bulk resistance obtained by the intercepts of the typical impedance curves  $Z'$  vs.  $Z''$ .

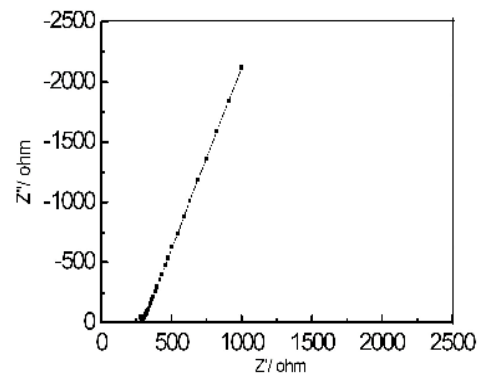


Fig2. Impedance plot for the film A2 with PVA-PEG-Mg(CH<sub>3</sub>COO)<sub>2</sub> : (40-50-10)

Fig 2. Show the nyquist plot for the film A2. The disappearance of the semicircular portion in the impedance curve leads to a conclusion that the current carriers are ions and this leads to one further conclude that the total conductivity is mainly the result of ion conduction [11]. The ionic conductivities were calculated using the relation  $\sigma = l/R_b A$ , where  $l$  is the thickness and  $R_b$  is the bulk resistance and  $A$  is the known area of the electrolyte film.

#### 3.3. Conductivity analysis

It has been observed that amorphous phase enhances higher ionic conduction and the crystalline phase provides strong mechanical support to the polymer electrolytes [12]. Table 1. Shows the composition and conductivity values of the polymer electrolytes. The sample A2 with 10 wt% of exhibits higher conductivity. As a general trend, in many studies for the dependence of salt concentration on the ionic conductivity in solid polymer electrolytes at low salt concentrations, the conductivity increases due to build up of charge carriers.

**Table1.** Conductivity values of PVA-PEG-Mg(CH<sub>3</sub>COO)<sub>2</sub> films with their composition

| Code | Composition<br>PVA-PEG- Mg(CH <sub>3</sub> COO) <sub>2</sub> | Conductivity<br>S/cm   |
|------|--------------------------------------------------------------|------------------------|
| A1   | 40-55-05                                                     | 6.256X10 <sup>-6</sup> |
| A2   | 40-50-10                                                     | 3.185X10 <sup>-5</sup> |
| A3   | 40-45-15                                                     | 1.311X10 <sup>-5</sup> |
| A4   | 40-40-20                                                     | 4.376X10 <sup>-6</sup> |
| A5   | 40-35-25                                                     | 9.642X10 <sup>-8</sup> |

At higher salt concentrations, the conductivity decreases due to build-up of charge carriers offset by the retarding effect of ion cloud.

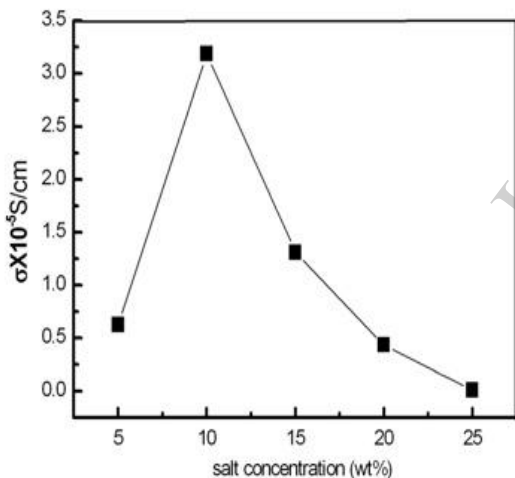
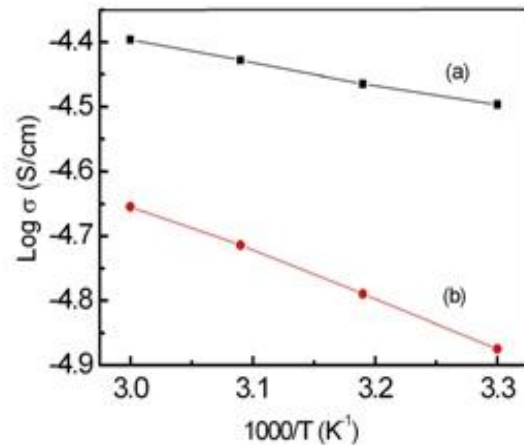


Fig3. Variation of conductivity with salt concentration

### 3.4 Temperature dependence conductivity

Measurement of ionic conductivity over a wide range of temperature is a good indicator of the thermal stability of the polymer electrolytes. Fig 4. shows the variation of conductivity against temperature for the samples A2 and A3. From the plot, it is evident that as the temperature increases, the ionic conductivity also increases for the electrolyte systems. The increase in conductivity with temperature may be due to the decrease in viscosity and hence increased chain flexibility [13].

Fig4. Temperature dependence of ionic conductivity of PVA-PEG-- Mg(CH<sub>3</sub>COO)<sub>2</sub> of film a) A2 (40-50-10), b) A3 (40-45-15)

The log  $\sigma$  versus  $1000/T$  curves follows a linear pattern, suggesting Arrhenius behaviour and thermally activated processes, which can be expressed as,  $\sigma = \sigma_0 \exp(-Ea /KT)$  where,  $\sigma_0$  is the pre-exponential factor,  $Ea$  is the activation energy and  $T$  is the absolute temperature in Kelvin scale [14]. The variation in conductivity with temperature has been explained in terms of segmental motion that results in an increase in free volume of the sample and hence motion of charge. The amorphous nature of composite blend provides a greater free volume of the system upon increasing temperature [15]. Thus segmental motion either permits the ions from one site to another or provides the pathways for ions to move. This inter-chain or intra chain ion movements are responsible for the high ionic conductivity in the electrolyte system

### . References

- [1] J.R MacCallum, C.a. Vincent, Polymer Electrolyte reviews-I&II, Elsevier, London, 1987 and 1989
- [2] F.M Gray, Solid Polymer Electrolytes-Fundamentals and Technological Applications, VCH, New York, 1991
- [3] R.C Agarwal,G.P Pandey, J.Phys.D:Appl.Phys.41 (2008) 223001
- [4] J.-M Tarascon, M. Armand, Nature 414 (2001) 359 [5] P.Novak, R. Imhof, O. Hass, Electrochim.Acta 45(1999) 351
- [6] A.Patrick, M.Glasse, R. Latham, R. Linford, Solid State Ionics 18&19 (1986)1063
- [7] G.P Pandey, R.C. Agarwal, S.A Hashmi J.Power Sources 190 (2009) 563
- [8] G.Girish Kumar, N.Munichandraiah Electrochimica Acta 47(2002)1013
- [9] K.Masuda, H. Kaji, F. Horii, J.Polym.Sci., Part B,Polym.Phys 38 (2000) 1

- [10] J.H Lee, H.B.Lee, J.D.Andrade, Prog.Polym.Sci 20 (1995) 1043
- [11] M.M.E. Jacob, S.R.S. Prabakaran, s.Radhakrishna, Solid State Ionics 104(1997) 267
- [12]AM Stephan,K.S Nahm, MA Kulandainathn,G.Ravi, J.Wilson (2006) J.Appl Electrochem 36: 1091
- [13] M.S Michael, MME Jacob, SRS Prabakaran,S.Radhakrishna (1997) Solid State Ionics 98:167
- [14] T.Aoki, T.Ohta, T.Fujinami (2006) J.Power Sources 156:589
- [15] K. Tsunemi, H. Ohno, E. Tsucida (1983) Electrochim Acta 28: 833

IJERT

IJERT