

XRD, Conductivity studies on PVA-PEG blend based Mg^{2+} ion conducting polymer electrolytes

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Abstract: Poly vinyl alcohol (PVA) and polyethylene glycol (PEG) blend based Mg^{2+} ion conducting polymer electrolytes have been prepared. Polyethylene glycol (PEG) with three different molecular weights 200,400 and 600 has been used and the effect of this molecular weight on the ionic conductivity of the electrolytes is studied through XRD, ac impedance technique. The analysis shows that the PEG with mol.wt 600 is more effective in reducing the crystallinity and enhancing the conductivity properties of the electrolytes.

Keywords: solid polymer electrolyte; pva-peg blend; xrd studies; ionic conductivity; magnesium nitrate

1. INTRODUCTION

Solid polymer electrolytes (SPE) has attracted considerable attention in terms of its scientific importance and application in energy storage or conversion devices such as batteries, fuel cells, super capacitors etc., arising from its high ionic conductivity, electrochemical stability and good mechanical properties [1-2]. Apart from lithium salt complexes, some other electrolytes are also reported containing salts of sodium, magnesium and zinc metals [3-5]. Presently the world wide attention has focused on the high performance and environment friendly nature of energy storage devices. Lithium ion conducting polymer electrolytes are incorporated in most of the commercially available batteries for their fabrication due to its high capacity and excellent chemical stability. At the same time lithium ion batteries are relatively expensive and suffer from safety limitations because of its explosive nature.

Magnesium ion based rechargeable batteries may serve as best alternative to lithium ion batteries. In the electromotive force series magnesium with an electrode potential of -2.3 V versus SHE is positioned next to lithium and its electrochemical equivalence (2.2 Ahg^{-1}) is also high. Studies on solid state rechargeable magnesium batteries are interesting in comparison with lithium batteries on account of the following advantages. i) Magnesium metal 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. Therefore safety problems associated with magnesium metal are minimal. ii) the ionic radii of Li^+ and Mg^{2+} are comparable in magnitude [6] iii) natural sources of magnesium are plentiful and thus it is cheaper than lithium.

Owing to these merits, investigations on electrochemistry of Mg-based rechargeable battery systems assume significant importance. Hence investigations on Mg^{2+} -ion conducting SPE are important. In the present communication, we have studied the effect of molecular weight of Poly ethylene glycol (PEG) on the ionic conductivity of the PVA-($MgNO_3$)₂ polymer electrolyte through xrd and ac impedance analysis. PVA is chosen because of its high tensile strength, electrochemical stability, good abrasion resistance and it can be easily blended with other polymers [7]. It contains carbon chain backbone with hydroxyl groups attached to methane carbons. The OH groups can be a source of hydrogen bonding hence the assistance in the formation of polymer blends [8-10].

2. Experimental

Poly vinyl alcohol (PVA) of molecular weight 1,25,000 and polyethylene glycol (PEG) with three different molecular weights 200,400 and 600 were purchased from CDH, India. Magnesium nitrate ($MgNO_3$)₂ was purchased from Merck, Germany. The magnesium salt was dried at 40°C for 24 h before using it. The wt% of PVA was kept constant for all compositions and the wt% PEG and ($MgNO_3$)₂ was varied so that the total wt% PEG+($MgNO_3$)₂ remains same. The required quantity PVA was dissolved in doubly distilled water. The appropriate quantity of magnesium salt was dissolved separately in distilled water and these two solutions were mixed. To this PEG was added and the mixture was continuously stirred for 10-12 h and resulting homogeneous solution was poured on cleaned Petri dishes and evaporated slowly at room temperature under vacuum to ensure removal of the solvent traces. After drying, the films were kept in vacuum desiccators for further characterization. The films were prepared with three different molecular weight PEG having same compositions.

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 powerful tool to determine the structure and crystallization of the polymer matrices. In order to investigate the effect of blending, XRD analysis has been performed and their respective diffraction patterns of pure and complex system are compared. Fig 1. shows the XRD patterns of pure PVA, PEG, ($MgNO_3$)₂ and the polymer membranes with PEG molecular weight 200,400 and 600. Fig 1.a shows the broad peak at $2\theta=20^\circ$ which shows the amorphous nature of the polymer PVA. The peaks pertaining to PEG ($2\theta=19.2^\circ$ & 23.4°) are shown in Fig1.b. The sharp peaks at $2\theta=16^\circ$, 27° , 29° , and at 49° reveal the crystalline nature of the salt. The fig 1d, e and f show the diffraction pattern of the membranes with PEG having molecular weight 200,400 and 600. The peaks related to ($MgNO_3$)₂ are found disappearing in the polymer electrolyte system indicating the salt is completely solvated with host polymers. There is a

significant change in the diffraction pattern of the film with PEG m.wt 600, the peak appears broader indicating the reduction in crystallinity of the system. Thus it is evident that PEG 600 has better plasticizing effect than the other two with lower molecular weight. PEG act as both as a blend polymer as well as plasticizer.

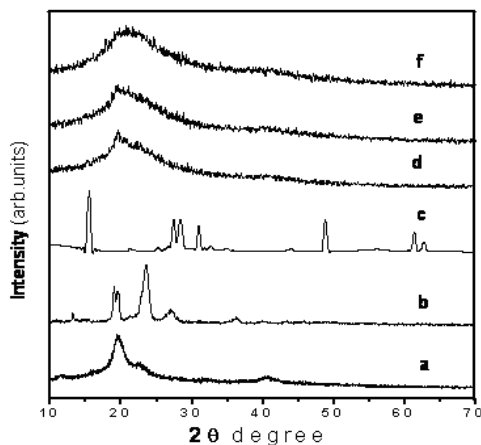


Fig1. X-ray diffraction patterns of (a) PVA (b) PEG (c) $(MgNO_3)_2$, film with (d) PEG 200 (e) PEG 400 (f) PEG 600

3.2 Impedance analysis

Impedance spectroscopy is a relatively new and powerful method for characterizing many of the electrical properties of electrolyte material and their interfaces with electronically conducting electrodes. It is carried out to establish the conduction mechanism, observing the participation of the polymeric chain, mobility and charge carrier generation processes. The prepared samples were sandwiched between the two stainless steel electrodes specially designed with spring attached to exert a small pressure to ensure good contact. A plot of negative imaginary impedance versus real impedance on a graph with vertical and horizontal axes gives a semicircle. From the complex impedance plot, the bulk resistance (R_b) can be obtained from the intercept of the curve on the real axis. By knowing the bulk resistance along with the dimensions of the sample, one can calculate the conductivity of the sample using the relation; $\sigma = l/R_b A$ where l and A are the thickness and area of the samples respectively. The conductivity measurements were carried out at four different temperatures from 303 K to 333 K. An impedance plot, real vs. imaginary parts of impedance for the film A2 (PVA-PEG₆₀₀-(MgNO₃)₂: 40-50-10) is shown in FIG2. The absence of semicircle portion in the impedance curve leads to a conclusion that the current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction [11].

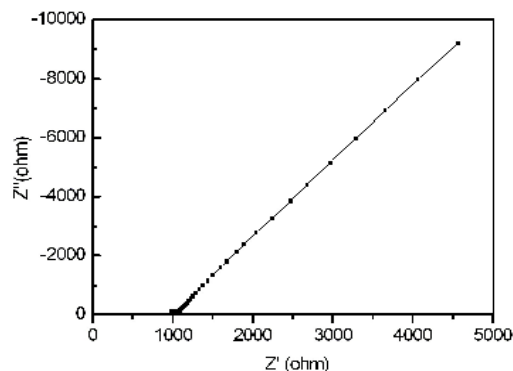


Fig 2. Impedance plot of the film A2 (PVA-PEG-(MgNO₃)₂: (40-50-10)

3.3 Conductivity analysis

Measurement of ionic conductivity over a wide range of temperature is a good indicator of the thermal stability of the polymer electrolytes. Fig 3. shows the conductivity of the samples with PEG 600 at different temperature. From the plot it is evident that as the temperature increases, the ionic conductivity also increases for the electrolyte systems. The increase in the conductivity with temperature may be due to the decrease in viscosity and hence increase d chain flexibility. The log vs. 1000/T curves for the electrolyte system shows a linear pattern ,suggesting Arrhenius behavior and thermally activated processes, which can be expressed as $\sigma = \sigma_0 \exp(-E_a/KT)$ where, σ_0 is the pre-exponential factor, E_a is the activation energy and T is the absolute temperature in Kelvin scale. When temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and crate a small amount of space surrounding its own volume in which vibrational motion can occur [12].Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence the conductivity. Hence, the increment of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobility.

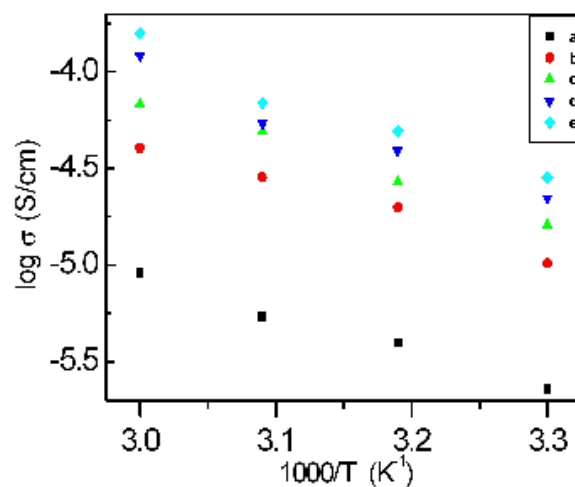


Fig3. Temperature dependence of ionic conductivity of PVA-PEG-(MgNO₃)₂ : a.(40-55-5), b.(40-50-10), c.(40-45-15) d. (40-40-20) e.(40-35-25)

4. Conclusions

Poly vinyl alcohol (PVA) and polyethylene glycol (PEG) blend based Mg^{2+} ion conducting polymer electrolytes have been prepared. Polyethylene glycol (PEG) with three different molecular weights 200,400 and 600 has been used and the effect of this molecular weight on the ionic conductivity of the electrolytes is studied through XRD, ac impedance technique. The analysis show that the PEG with m.wt 600 is more effective in reducing the crystallinity and thus enhancing the Conductivity.

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