

Mg²⁺-Ionic Conductivity Behavior of Mixed Salt System in PVA-PEG Blend Matrix

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Abstract- Poly vinyl alcohol(PVA) and Poly ethylene glycol (PEG) blend based polymer electrolytes has been prepared using Mg(CH₃COO)₂ and Mg(NO₃)₂ as salt by varying the PEG: [Mg(CH₃COO)₂ and Mg(NO₃)₂] ratio. The ionic conductivity of the prepared films was studied through XRD and AC impedance techniques. The temperature dependence conductivity shows Arrhenius behavior. The maximum conductivity of 9.852X10⁻⁶ S/cm was observed for the film with composition PVA-PEG- [Mg(CH₃COO)₂ +Mg(NO₃)₂]: (40-45-7.5-7.5)

Index Terms- Ionic conductivity, mixed salt system, PVA-PEG polymer blend, Xrd studies

I. INTRODUCTION

Ion conducting polymer electrolytes are of a major global interest to physicist, chemists and engineers as they offer a better substitute to liquid electrolytes because of their potential application in various electrochemical devices particularly in batteries and super capacitors[1-2]. It has been accepted that polymer gel electrolytes possess some distinct advantages over liquid electrolytes, such as reduced reactivity, reduced leakage, improved safety and better shape flexibility. The world wide attention has focused on the high performance and environment-friendly nature of the energy storage devices. Lithium ion is incorporated in most of the commercially available batteries for their fabrication due to its high specific capacity and excellent cyclic stability [3-4]. But the problem faced with lithium such as difficulty in handling in open ambience due to high reactivity and high cost has directed towards the search of other substitutes. Few reports appeared on silver and divalent ion conducting polymer electrolytes [5-6]. However less attention has been given to solid polymer electrolytes based on magnesium complex systems. The magnesium metal is more stable and cheaper than lithium. Magnesium is an attractive electrode material. It is employed as the negative electrode in primary batteries, which are based on aqueous electrolytes. Several methods, such as copolymerization, plasticization, blending and addition of fillers have been used to enhance the conductivity of the polymer electrolytes. Among these blending of polymer s is a useful tool to develop new polymeric material with improved mechanical stability. The main advantages of the blend system are simplicity of preparation and ease of control of physical properties by compositional changes [7]. Most studies have been on high molecular weight polymers (eg. PEO) complexed with alkali metal salts (lithium being the most studied). However not much attention has been paid to the low molecular weight PEO or PEG.

In the present work, Poly vinyl alcohol (PVA) was blended with polyethylene glycol (PEG) and mixed salt system is used as conducting species. Kanbara et al. [8] studied the PVA based lithium salts complexed electrolytes for the application in electric double layer capacitors. Magnesium acetate Mg(CH₃COO)₂ and magnesium nitrate Mg(NO₃)₂ were mixed in equal wt% and used as the salt for this system. The polymer electrolytes were subjected to xrd and ac impedance analysis to optimize the composition and conductivity of the electrolytes.

II. EXPERIMENTAL

Poly vinyl alcohol (PVA) with average molecular weight 1,25,000 and poly ethylene glycol (PEG) with average molecular weight 400 were purchased from CDH, India. PVA was first dissolved separately in minimum amount of doubly distilled water. The salts were magnesium acetate and magnesium nitrate were dissolved in another beaker after complete dissolution these two solutions were mixed stirred at room temperature. To this required quantity of PEG was added and the solution was stirred continuously for about 10-12 h. The resulting homogeneous viscous liquid was then cast on ultrasonically cleaned glass plates. The residual solvent was allowed to evaporate slowly at room temperature under vacuum to ensure complete removal of the solvent traces. After drying, the films were peeled off and kept in vacuum desiccators till further characterizations. The thickness of the thus prepared film varies between 90-120 μm. The wt% of PVA was kept constant for all the electrolyte membranes and wt% of PEG and mixed salts was varied to investigate its effect on the conductivity behavior of the electrolyte membranes.

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.

III. RESULTS AND DISCUSSIONS

A. 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(CH₃COO)₂ system XRD analysis has been performed and their respective diffraction patterns of pure PVA, PEG, Mg(CH₃COO)₂, Mg(NO₃)₂ and the film with composition (PVA-PEG- Mg(CH₃COO)₂-Mg(NO₃)₂ : 40-50-7.5-7.5) 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°) are shown in Fig1.b. The peaks corresponding to Mg(CH₃COO)₂ at $2\theta = 20.8, 27.7, 32.3^\circ$ disappear in the electrolyte film indicating that the salt is completely solvated by the host polymer. Similarly the absence of peaks of magnesium nitrate salt shows that it is solvated by the constituents of the system. The suppression the peak corresponding to PVA show that the decrease in the crystallinity of the complex. These changes reveal clearly that the polymer electrolyte is predominantly amorphous and its crystallinity is depressed due to the addition of PEG. This indicates that the PEG most likely blends with PVA at the molecular level and functions as a both blend polymer as well as plasticizer. This feature is needed as the ion conduction takes place in the amorphous region.

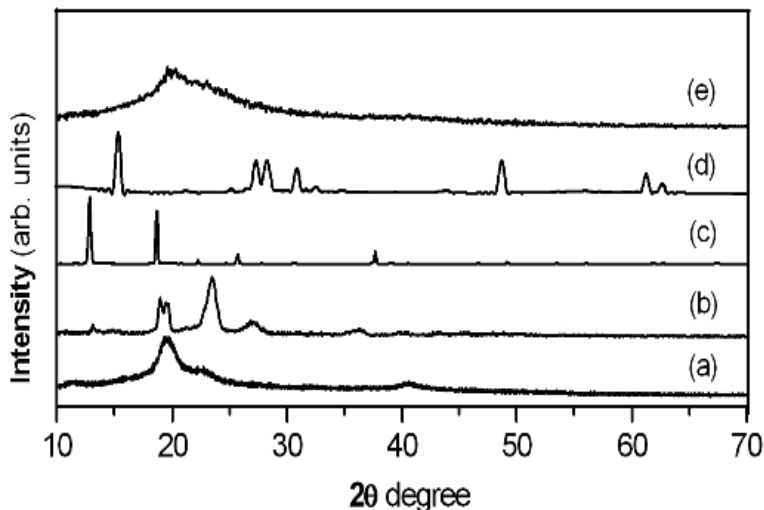


Fig1. X-ray diffraction patterns of (a) PVA, (b) PEG, (c) Mg (CH₃COO)₂, (d) Mg(NO₃)₂, and (e) film with composition PVA- PEG- [Mg(CH₃COO)₂- Mg(NO₃)₂]: [40-45-(7.5-7.5)]

B. 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. This method is employed to establish the conduction mechanism, observing the participation of the polymer chain, mobility and carrier generation processes. The solid polymer blend electrolytes were sandwiched between two stainless steel electrodes specially designed with spring attached to one to exert a small pressure between the film and the electrode 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 room temperature. The film exhibiting higher conductivity was subjected to impedance measurement at four different temperatures from 303 K to 333 K. An impedance plot, real vs. imaginary parts of impedance for the film A3, PVA- PEG- Mg(CH₃COO)₂- Mg(NO₃)₂: (40-45-7.5-7.5) is shown in FIG2. The disappearance of the semicircular 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 [9].

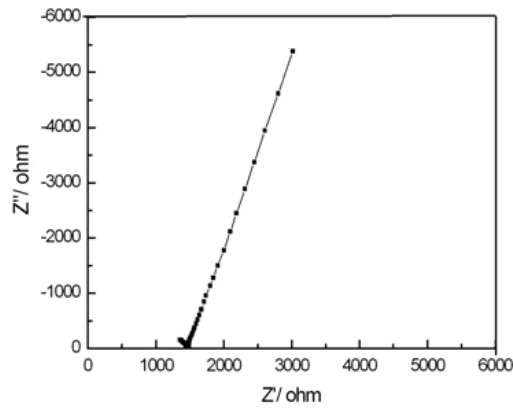


Fig 2. Impedance plot of the film A3, PVA- PEG- [Mg (CH₃COO)₂- Mg(NO₃)₂]: [40-45-(7.5-7.5)]

C. Conductivity analysis

Table 1: shows the conductivity values of the electrolyte membranes with their composition at room temperature. The film with 7.5 wt% of Mg(CH₃COO)₂ and 7.5 wt% Mg(NO₃)₂ exhibits higher conductivity than others.

Table 1: Conductivity values of the polymer electrolytes with their composition

code	PVA- PEG- Mg (CH ₃ COO) ₂ - Mg(NO ₃) ₂ : (40-45-7.5-7.5)	conductivity S/cm
A1	40-55-2.5-2.5	5.051X10 ⁻⁶
A2	40-50-5-5	7.816X10 ⁻⁶
A3	40-45-7.5-7.5	9.852X10 ⁻⁶
A4	40-40-10-10	7.767X10 ⁻⁶
A5	40-35-12.5-12.5	6.434X10 ⁻⁶

The same behavior is plotted in Fig3. salt concentration vs. conductivity. Jeon et al. [10] reported that the conductivity of the polymer electrolytes increased with increasing salt concentration, but further addition of the salt caused the conductivity to decrease.

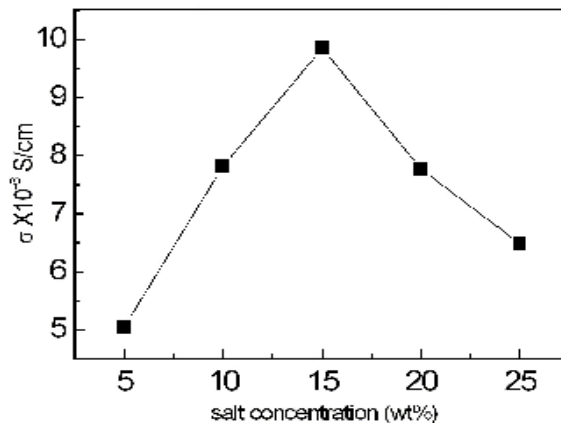


Fig 3: Effect of salt concentration on the conductivity of the electrolytes

MacCallum et al. explained that the conductivity increases initially with increasing salt concentration as the number of charge carriers increases, but at higher salt concentrations, the conductivity decreases because of the increasing influence of ion pairs, ion triplets, and higher ion aggregations, which reduces the overall mobility and number of the effective charge carriers.

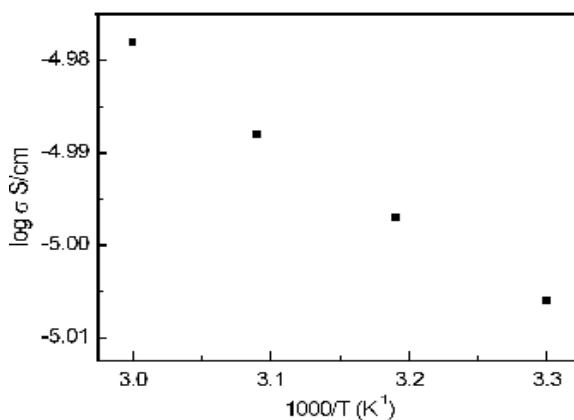


Fig 4: Temperature dependence of ionic conductivity of the film with composition A3,

PVA- PEG-[Mg (CH₃COO)₂- Mg(NO₃)₂] : [40-45-(7.5-7.5)]

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 temperature-dependent conductivity of the polymer electrolyte with higher conductivity. The impedance measurements were carried out from temperature ranging from 303 K to 333 K. 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 increased 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. Miyamoto and Shibayama [11] explained that the ionic conductivity increased with increasing temperature as result of the free volume model where as the temperature increases, the polymer electrolyte can expand easily and produce free volume. Therefore ions solvated molecules or polymer segments can move into the free volume causing it to increase [12]. This enhances the ion and the polymer segmental mobility which will in turn enhance the conductivity.

IV CONCLUSIONS

Poly vinyl alcohol (PVA), Poly ethylene glycol (PEG) blend based polymer electrolytes with Mg(CH₃COO)₂ and Mg(NO₃)₂ as salt has been prepared. The Xrd and conductivity analysis reveal that the PEG and salt concentration greatly affects the conductivity of the electrolyte. As the magnesium metal is cheaper and less toxic when compared to lithium it could be a better alternative to lithium. Studies towards fabricating non aqueous electrolytes with different magnesium salts to enhance the conductivity, mechanical and thermal stability are in progress.

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