Ionic conductivity and electrochemical cell studies of new Mg^{2+} ion conducting PVA/PEG based polymer blend electrolytes

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ABSTRACT

Solid Polymer blend electrolytes based on Polyvinyl alcohol (PVA) and Polyethylene glycol (PEG) complex with $Mg(CH_3COO)_2$ at different weight percent ratios were prepared using solution cast technique. Conductivity in the temperature range 303-373 K and transference number measurements have been employed to investigate the charge transport in this solid polymer electrolyte system. The highest conductivity is found to be 3.23 x 10^{-5} S/cm at 373K for sample with 30 weight percent of $Mg(CH_3COO)_2$ in PVA/PEG blend matrix. Transport number data shows that the charge transport in this polymer electrolyte system is predominantly due to ions. Using this electrolyte, an electrochemical cell with configuration Mg /(PVA+PEG+Mg(CH$_3$COO)$_2$)/ (I$_2$+C+electrolyte) was fabricated and its discharge characteristics profile has been studied. Copyright © 2012 VBRI Press.

Keywords: Polymer electrolytes; ionic conductivity; transport number; discharge characteristics.

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Introduction

Solid polymer electrolytes have been a subject of great interest in recent years due to their potential applications in rechargeable batteries, fuel cells, sensors, electrochromic display devices, smart windows and other applications [1, 2]. Compared with systems based on liquid or gel electrolytes, solid polymer electrolytes are much more stable and have long life characteristics. The properties of polymer composites have been studied by various researchers [3-9]. Poly (ethylene) oxide (PEO) has been a

popular choice of polymer matrix for magnesium ion conductors [10-13], but very less work has done based on polymer blends. Polymer blending is one of the most important contemporary ways for the development of new polymeric materials and it is a useful technique for designing materials with a wide variety of properties [14]. The significant advantages of polymer blends are often exhibit properties that are superior compared to the properties of each individual component polymer [15]. However, the manifestation of superior properties depends upon the miscibility of blend. Blending can, however, have profound and sometimes unexpected effects on thermal stability, which cannot simply be predicted on the basis of behavior of the components and their relative proportions [16].

Many types of solid polymer electrolytes (SPEs) have been proposed based on organic polymer matrixes which dissolved inorganic salts, especially such alkali metal salts. Contrarily, little has been published for materials in which multivalent (divalent, trivalent, or tetravalent) cations are the mobile species [17]. Indeed, materials showing Mg^{2+} conductivity are quite interesting due to the following advantages:

1) The ionic radii of Li^+ and Mg^{2+} are 68 and 65 pm, respectively, i.e., comparable in magnitude. Hence, easy replacement of Li^+ ions by Mg^{2+} ions in insertion compounds is possible.

2) Magnesium metal is more stable than the 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.

3) Global raw material resources of magnesium are plentiful and thus, it is much cheaper than the lithium [18].

E.M. Abdelrazek has reported the physical properties of $MgCl_2$-filled PMMA films for optical applications [19]. Pandey et al has prepared magnesium ion conducting gel polymer electrolytes dispersed with fumed silica for rechargeable magnesium battery application [20]. Chu and Jaipal Reddy studied the PEO-Mg polymer electrolyte system [12]. Vito Di Noto et al has done a research on Li and Mg polymer electrolytes based on esters of ethylenediaminetetraacetic acid and PEG400 [21].

In the present work, Mg^{2+} ion conducting polymer blend electrolytes based on Polyvinyl alcohol/poly (ethylene glycol) complexed with $Mg(CH_3COO)_2$ were prepared by using a solution casting technique. Several experimental techniques such as electrical and transport number measurements were performed to characterize these polymer electrolytes. Based on these electrolytes, electrochemical cells were fabricated with anode/polymer electrolyte/cathode configuration. The discharge characteristics of the cell were studied for a load of 100 kΩ.

Experimental

Materials

Polyvinyl alcohol (PVA) from CDH, India has molecular weight 1,25,000 and polyethylene glycol (PEG) from CDH, India has molecular weight 4,000 were dried at 50°C and 40°C under vacuum for 48 hours, respectively. Magnesium acetate ($Mg(CH_3COO)_2$) (98%, CDH, India) was dried

under vacuum for 24 h at 40 °C. The solvent used in this work was distilled water.

Polymer electrolyte preparation

Solid polymer blend electrolyte films were prepared using the solution cast technique. Equal quantity of PVA and PEG (50/50) by weight was added to doubly distilled water with stirring the solution at room temperature to complete dissolution. Required quantity (0, 10, 20, 30 and 40 wt. %) of $Mg(CH_3COO)_2$ was also dissolved in doubly distilled water and added to the polymeric solution with continuous stirring for about 12 hours. The solution was poured into cleaned Petri dishes and evaporated slowly at room temperature under vacuum to ensure removal of the solvent traces. After drying, the films were peeled from Petri dishes and kept in vacuum desiccators until use. The thickness of the obtained films was in the range of 90-120 μm.

Characterization

When the polymer electrolyte films have formed they were placed between the blocking stainless steel electrodes of the conductivity cell with leads connected to a HIOKI 3532-50 LCR meter interfaced to a computer for conductivity measurements. The measurements were made over a frequency range of 42Hz to 5MHz at different temperatures. The temperature dependent conductivity studies were carried out for PVA-PEG-30 wt. % of $Mg(CH_3COO)_2$ polymer electrolyte films. Conductivity measurements were carried out over the same frequency range for temperatures ranging from room temperature to 373 K. The conductivity cell with connecting lead wires were placed in an oven with temperature control facilities.

The transference number measurements were made using Wagner's polarization technique [22]. Using the polymer electrolyte films, solid-state electrochemical cells have been fabricated with the configuration $Mg/(PVA+PEG+Mg(CH_3COO)_2)/(I_2+C+electrolyte)$ under a constant load of 100 kΩ.

Results and discussion

Conductivity studies

The ionic conductivity of polymer electrolytes as a function of magnesium acetate concentration at 303K and 373K are presented in **Fig. 1**. The ionic conductivity of different compositions of PVA-PEG-$Mg(CH_3COO)_2$ complexes are given in **Table 1**. The maximum ionic conductivity of 3.23×10^{-5} S/cm was obtained for the system PVA–PEG–$Mg(CH_3COO)_2$ (50–50–30) at 373K. Jeon et al. [23] reported that the conductivity of polymer electrolytes increased with increasing salt concentration, but further addition of the salt caused the conductivity to decrease. MacCallum *et al*. [24] 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 the number of effective charge carriers. The temperature dependence of ionic conductivity of PVA-PEG

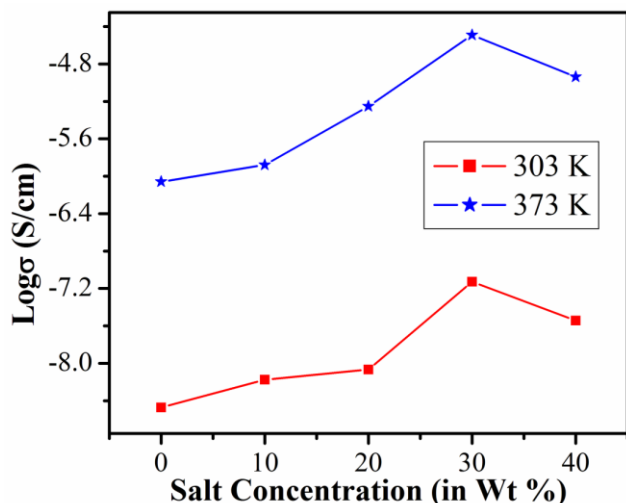polymer blend complex with 30 wt % of Mg(CH₃COO)₂ is shown in **Fig. 2**.

Fig. 1. Salt concentration vs logσ plots of PVA-PEG-Mg(CH₃COO)₂ polymer system at different temperatures.

Table 1. Ionic conductivity values of PVA-PEG-Mg(CH₃COO)₂ solid polymer blend electrolytes at various temperatures.

Sample PVA-PEG-Mg(CH₃COO)₂	Ionic conductivity in S/cm	
	303 K	373 K
50-50-00	3.38×10^{-9}	8.71×10^{-7}
50-50-10	6.69×10^{-9}	1.32×10^{-6}
50-50-20	8.58×10^{-9}	5.58×10^{-6}
50-50-30	7.44×10^{-8}	3.23×10^{-5}
50-50-40	2.86×10^{-8}	1.15×10^{-5}
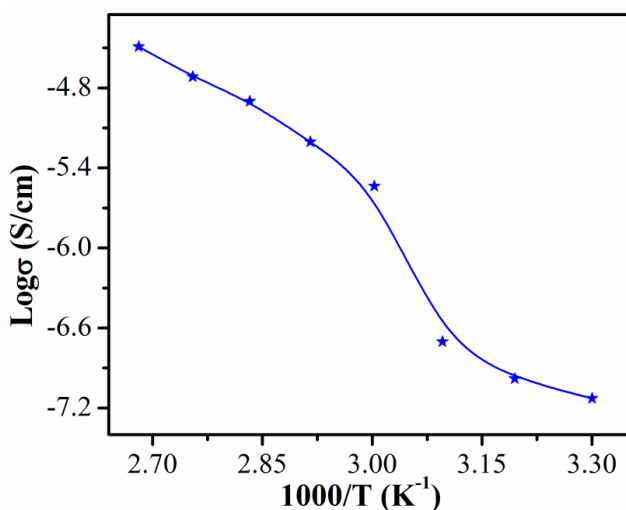
Fig. 2. Temperature dependent conductivity of PVA-PEG-30 wt % of Mg(CH₃COO)₂ solid polymer blend electrolyte.

The curvature shown in this plot indicates that the ionic conduction obeys the VTF relation which describes the transport properties in a viscous matrix **[25, 26]**. It is found that as temperature increases, the conductivity values also increase for all the compositions. As the temperature

increases, the polymer can expand easily and produce free volume. Thus ions, solvated molecules or polymer segments may move in to the free volume. The resulting conductivity is represented by overall mobility of ion and polymer which is determined by the free volume around polymer chain. The increase in free volume leads to the increase in ion mobility and segmental mobility that will assist the ion transport.

Transport number studies

The ionic transference number of the mobile species in the polymer electrolyte was calculated by Wagner's dc polarization technique **[22]**. This method was used to analyze the mobile species in the electrolyte. The polarization current was monitored as a function of time on the application of dc potential (1.5 V) across the cell in the configuration Mg/(PVA+PEG+Mg(CH₃COO)₂)/C is shown in **Fig. 3**. The current decays immediately and asymptotically approaches steady state.
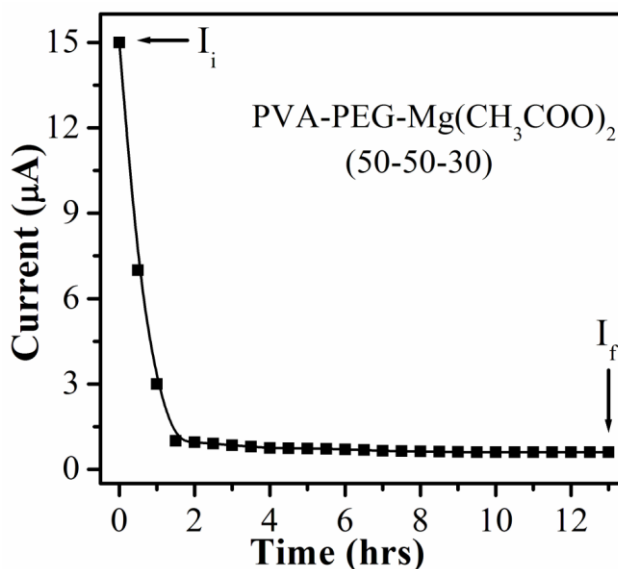

Fig. 3. Current versus time plot of PVA-PEG-Mg(CH₃COO)₂ (50-50-30) solid polymer blend electrolyte

The total ionic transference number was calculated from the polarization current vs time plots using the standard equation

$$t_{ion} = 1 - \frac{I_f}{I_i}$$
$$t_{ele} = 1 - t_{ion}$$

where I_i is the initial current and I_f is the final residual current.

The total ionic transference number was found to be ~ 0.96 in this polymer electrolyte system. This suggests that the charge transport in these polymer electrolytes is predominantly due to ions.

Battery discharge studies

Fig. 4 shows the discharge characteristics of the electrochemical cell Mg/(PVA+PEG+ Mg(CH₃COO)₂) (50-50-30)/ (I₂+C+electrolyte) for a constant load of 100 kΩ.

The initial sharp decrease in the voltage in these cells may be due to polarization and/or the formation of a thin layer of magnesium salt at the electrode-electrolyte interface. The cell parameters for these cells were evaluated and are listed in **Table 2**.
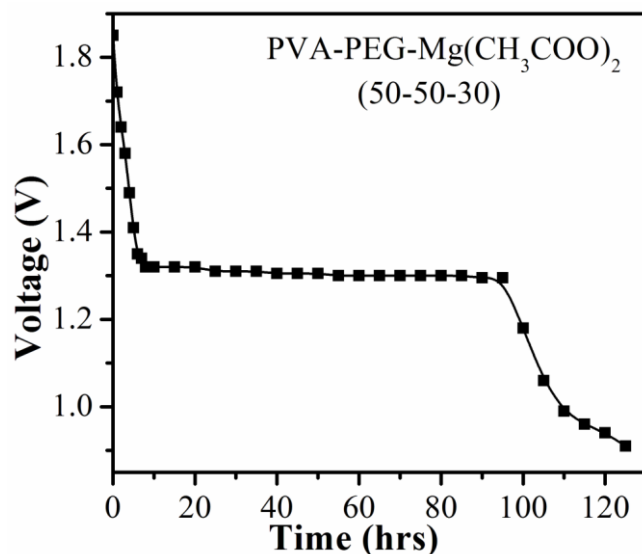

Fig. 4. Discharge characteristics of PVA-PEG-Mg(CH$_3$COO)$_2$(50-50-30) electrochemical cell (load = 100 kΩ).

Table 2. Cell parameters of [PVA-PEG-Mg(CH$_3$COO)$_2$] (50-50-30) electrolyte cell at a constant load of 100 kΩ.

Cell parameters	Mg/(PVA + PEG + Mg(CH$_3$COO)$_2$) (50-50-30)/ (I$_2$+C+electrolyte)
Cell weight	1.48 g
Area of the cell	1.33 cm^2
Open circuit voltage (OCV)	1.84 V
Discharge time for plateau region	88 h
Current density	13.84 µA/cm^2
Discharge capacity	1.62 m A h
Power density	16.16 m W/Kg
Energy density	2.02 W h/Kg

Conclusion

The PVA+PEG+Mg(CH$_3$COO)$_2$ polymer blend electrolyte films are prepared successfully. The maximum ionic conductivity of polymer salt complex is found to be ~ 3.23 x 10^{-5} S/cm at 373K. The temperature dependent conductivity of polymer electrolytes obeys the VTF behavior. The conducting species in the polymer electrolyte system was found to be predominantly ions. The electrochemical cell results show that (PVA+PEG+Mg(CH$_3$COO)$_2$) system is a potential candidate for fabrication of solid state batteries.

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