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# Effect of $Al_2O_3$ ceramic filler on PEG-based composite polymer electrolytes for magnesium batteries

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## ABSTRACT

Composite polymer electrolyte films consisting of polyethylene glycol (PEG), $Mg(CH_3COO)_2$ and $Al_2O_3$ particles have been prepared by solution casting technique. The X-ray diffraction patterns of PEG-$Mg(CH_3COO)_2$ with $Al_2O_3$ ceramic filler, indicates the decrease in the degree of crystallinity with increasing concentration of the filler. The role of ceramic phase is to reduce the melting temperature which is ascertained from the DSC. The effect of ceramic filler on the conductivity of the polymer electrolyte was studied. The maximum ionic conductivity has been observed for 10 wt% of $Al_2O_3$ at room temperature (303 K). The transference number data indicated the dominance of ion-type charge transport in these composite polymer electrolytes. Using this (PEG-$Mg(CH_3COO)_2$-$Al_2O_3$) (85–15–10) electrolyte, solid-state electrochemical cell was fabricated and their discharge profiles were studied under a constant load of 100 kΩ. Several cell profiles associated with this cell were evaluated and are reported. Copyright © 2013 VBRI press.

**Keywords:** Composite polymer electrolytes; PEG; transference number; electrochemical cell; ceramic filler.

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## Introduction

There has been a lot of interest on research and development of solid state electrochemical devices such as rechargeable batteries, capacitors and sensors, which employ a thin film of solid polymer as an electrolyte material **[1]**. Among the electrochemical devices, polymer electrolytes have been widely studied and developed for battery applications over the past 33 years. Composite polymer electrolytes (CPEs) comprising of a polymer host, doping salt and inorganic / ceramic filler were first demonstrated by Weston and Steele in 1982 **[2]**. The properties of polymer composites have been studied by various researchers **[3-10]**. The addition of fillers into the polymer matrixes improves both the mechanical strength of the polymer **[2, 11]** and their ionic conductivities **[12]**. The additives used include $SiO_2$ **[13]**, $ZrO_2$ **[14]**, $TiO_2$ **[15]**, $CeO_2$ **[16]**, $Al_2O_3$ **[17]** etc., and in most work on composite polymer electrolytes, the electrolyte is usually based on high molecular weight PEO **[2, 11, 17]**. Little attention has been paid to the somewhat low molecular weight polymers. Bearing these facts in mind, we have prepared and published our previous work with poly (ethylene glycol) (PEG) of molecular weight 4000, complexed with $Mg(CH_3COO)_2$ salt **[18]**.

In present paper, we report the composite solid polymer electrolytes prepared by the addition of $Al_2O_3$ particles to

PEG-$Mg(CH_3COO)_2$ (85-15). The purpose of this work is to emphasis the extraordinary effect occurring in the PEG-$Mg(CH_3COO)_2$-$Al_2O_3$ composite polymer electrolytes. Our results demonstrate that the dispersion of $Al_2O_3$ particles in the PEG-$Mg(CH_3COO)_2$ matrix leads to an increase in the ionic conductivity of the composite polymer electrolytes. The resultant electrolyte films have been characterized by XRD, DSC analyses. The conductivity of the polymer electrolytes is measured using ac impedance technique in the temperature range 303-333 K.

## Experimental

### *Materials*

PEG (99%, average molecular weight 4,000) purchased from CDH, India, was dried at 40°C for 5 h; Magnesium acetate ($Mg(CH_3COO)_2$) (98%, CDH, India) was dried under vacuum for 24 h at 40°C and $Al_2O_3$ procured from LOBA Chemie, India (99.6%) was used. The solvent used in this work was distilled water.

### *Polymer electrolyte preparation*

Solid polymer electrolyte samples were prepared using the solution cast technique. PEG (molecular weight of 4,000) was used as the polymer. $Mg(CH_3COO)_2$ was added accordingly. The solvent used in this work is distilled water. The mixture was stirred up to 10 hours to obtain a homogeneous solution. After incorporating the required amount of inorganic filler ($Al_2O_3$ powder) was suspended in the solution and stirred for about 10 h. The solution was then poured into the glass petri dishes and evaporated slowly at room temperature under vacuum. The polymer electrolyte samples were then transferred into desiccators for further drying before the test.

### *Characterization*

In order to investigate the nature of these polymer electrolyte films, WAXD patterns were recorded in the diffraction angular range 10-60° 2θ by a Philips X'Pert PRO (Almelo, The Netherlands) diffractometer, working in the reflection geometry and equipped with a graphite monochromator on the diffracted beam (CuKα radiation). The thermal response was studied by Differential Scanning Calorimetry (TA Instruments model 2920 calorimeter) in the static nitrogen atmosphere at a heating rate of 5°C/min. in the temperature range 0 to 100°C. Impedance measurements were carried out in the temperature range 303-333 K using HIOKI 3532-50 LCR Hitester over a frequency range 42 Hz to 5 MHz. The transference number measurements were made using Wagner's polarization technique **[19]**. Solid-state electrochemical cells were fabricated in the configuration Mg/(PEG-$Mg(CH_3COO)_2$-$Al_2O_3$)/($I_2$+C+electrolyte). The discharge characteristics of the cells were monitored under a constant load of 100 kΩ.

## Results and discussion

### *XRD*

**Fig. 1** shows X-ray diffraction patterns of 85PEG-15$Mg(CH_3COO)_2$ polymer electrolyte with x wt% of $Al_2O_3$ (x = 0, 5, 10, 15, 20) and pure $Al_2O_3$. X-ray diffraction analysis shows the decrease of crystallinity of the composite polymer electrolytes in comparison to the electrolyte without $Al_2O_3$.

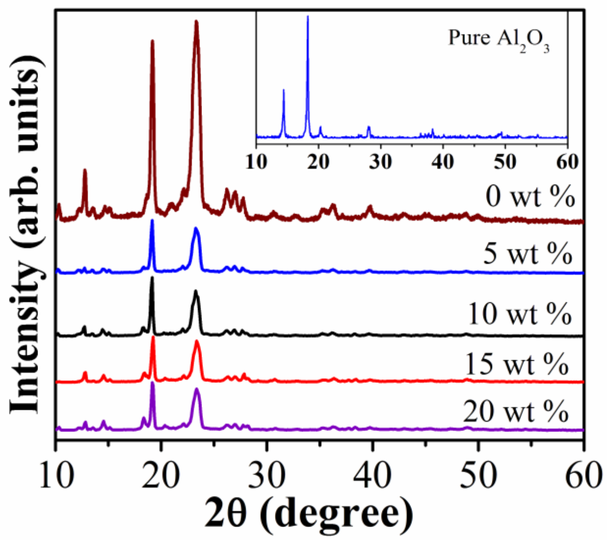

**Fig. 1.** X-ray diffraction patterns of 85PEG-15$Mg(CH_3COO)_2$- x wt% of $Al_2O_3$ CPEs (x = 0, 5, 10, 15 and 20) and pure $Al_2O_3$.

The intensities of crystalline peak of PEG in the vicinity of 19.2° and 23.4° has decreased remarkably according to the amount of $Al_2O_3$ introduced into the polymer electrolyte. In other words, volume fraction of amorphous phase in PEG polymer electrolyte increased with the amount of $Al_2O_3$ into the polymer matrix. Increased amorphicity in the composite polymer electrolyte membrane, which gives rise to higher conductivity, is attributed to addition of the filler. Dispersed phase submicron size filler particles prevent the polymer chain reorganization, resulting in reduction in polymer crystallinity which gives rise to an increase in ionic conductivity **[20]**.

### *DSC*

**Fig. 2** shows the DSC curves of 85PEG-15$Mg(CH_3COO)_2$ polymer electrolyte with x wt% of $Al_2O_3$ (x = 0, 5, 10, 15, 20) in the temperature range of 0-100 °C. The DSC studies for pure PEG are given in our previous paper **[21]**.

There is a characteristic endothermic peak on the order of 54-56 °C which is attributed to the melting point of crystalline PEG. The melting point of PEG of CPE is a little lower than the polymer electrolyte without $Al_2O_3$. By assuming that pure PEG was 100% crystalline, the relative percentage of crystallinity ($X_c$) was calculated based on the following equation with the DSC data.

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\ \% \qquad (1)$$

where $\Delta H_m^0$ is the standard enthalpy of fusion of pure PEG, 204.3 J/g and $\Delta H_m$ is enthalpy of fusion of the composite polymer electrolyte. $X_c$, $\Delta H_m$ and the crystalline melting temperature ($T_m$) for all CPEs are presented in **Table 1**. From the **Table 1** and **Fig. 2**, it is clear that melting temperature ($T_m$) and crystallinity ($X_c$) are decreasing with the addition of $Al_2O_3$ content up to 10wt% and then slightly increases in the CPE systems.

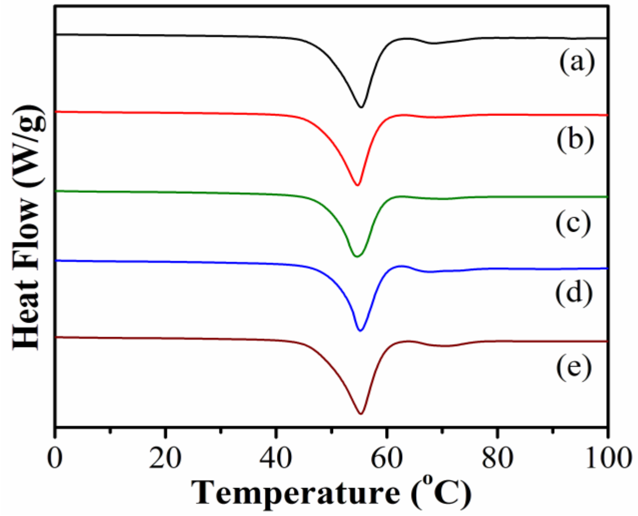

**Fig. 2.** DSC curves of 85PEG-15Mg($CH_3COO$)$_2$- x wt% of $Al_2O_3$ CPEs a) 0 wt.%, b) 5 wt.%, c) 10 wt.%, d) 15 wt.% and e) 20 wt.%.

**Table 1.** DSC results.

| Sample | $Al_2O_3$ Concentration [in wt%] | Melting point ($T_m$) [°C] | $\Delta H_m$ [J/g] | $X_c$ (in %) |
|---|---|---|---|---|
| Pure PEG | | 59.42 | 204.3 | 100 |
| 85PEG-15Mg($CH_3COO$)$_2$ | 0 | 55.32 | 185.0 | 90.6 |
| 85PEG-15Mg($CH_3COO$)$_2$ | 5 | 54.73 | 153.4 | 75.1 |
| 85PEG-15Mg($CH_3COO$)$_2$ | 10 | 54.58 | 136.1 | 66.6 |
| 85PEG-15Mg($CH_3COO$)$_2$ | 15 | 55.14 | 162.8 | 79.7 |
| 85PEG-15Mg($CH_3COO$)$_2$ | 20 | 55.28 | 170.5 | 83.5 |

The reorganization of polymer chain may hinder by the cross-linking centers formed by the interaction of the Lewis acid groups of filler with the polar groups of polymer. As a result, the degree of crystallization of polymer matrix decreases with the addition of filler **[22]**. The addition of $Al_2O_3$ in the polymer electrolytes is more responsible to the segmental chain motion of the polymer. In addition, above 10 wt% of $Al_2O_3$ in the PEG matrix results in an increase in $T_m$, $\Delta H_m$ and $X_c$. It is ascribed to the increase of $Al_2O_3$ content above 10 wt% in the polymer matrix causes aggregation of particles which increase the crystallinity of the CPE membrane. This leads to lower segmental mobility and hence reduced ionic conductivity.

### *Conductivity studies*

The effect of filler content on the ionic conductivity of the PEG-Mg($CH_3COO$)$_2$ with $Al_2O_3$ at five different contents 0, 5, 10, 15 and 20 wt% was examined. The filler content dependence of the ionic conductivity in the composite polymer electrolytes at room temperature is shown in **Fig. 3**.

The ionic conductivity of the composite polymer electrolyte increased with an increase in filler content and reached a maximum value, then started decreasing with further addition of filler. The highest conductivity was obtained at the $Al_2O_3$ content of 10 wt%. The room temperature conductivity values are given in **Table 2**. The increase in conductivity has been attributed to: (i) the ceramic particles acting as nucleation centers for the formation of minute crystallites **[23]**; (ii) the ceramic particles aiding in the formation of amorphous phase in the polymer electrolyte **[24]**; (iii) the formation of the new kinetic path via polymer–ceramic boundaries **[25]**.

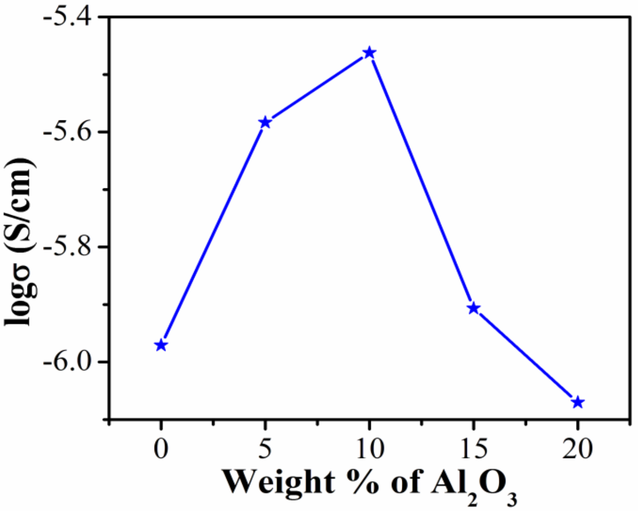

**Fig. 3.** Effect of the concentration of $Al_2O_3$ on the conductivity of 85PEG-15Mg($CH_3COO$)$_2$ polymer electrolyte at room temperature (303 K).

**Table 2.** Ionic conductivity and activation energy values of PEG-Mg($CH_3COO$)$_2$-$Al_2O_3$ CPEs.

| **Sample** | **Ionic Conductivity [S/cm] at 303 K** | **Activation Energy $E_a$ [eV]** |
|---|---|---|
| 85-15-00 | $1.07 \times 10^{-6}$ | 0.304 |
| 85-15-05 | $2.61 \times 10^{-6}$ | 0.138 |
| 85-15-10 | $3.45 \times 10^{-6}$ | 0.086 |
| 85-15-15 | $1.24 \times 10^{-6}$ | 0.285 |
| 85-15-20 | $8.51 \times 10^{-7}$ | 0.310 |

However, the conductivity is found to decrease after an optimum concentration of $Al_2O_3$ is crossed. As the optimum concentration is attained, on further addition of filler a continuous non-conductive phase build up by large amount of fillers as an electrically inert component would block up Mg-ion transport, resulting in an increase in total resistance of the composite polymer electrolyte. It is reported for many composite polymer electrolytes formed by the addition of filler that ionic conductivity increases to reach its maximum value at 5–10 wt% of filler **[26, 27]**.

**Fig. 4** shows the conductivity (log σ) vs. temperature inverse plots of PEG-$Mg(CH_3COO)_2$- $Al_2O_3$ composite polymer electrolyte system with varying the filler concentration. From **Fig. 4**, it is observed that the conductivity versus temperature behavior of the system is linear, i.e. follows Arrhenius relationship,

$$\sigma = \sigma_0 exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

where $\sigma_0$ is the pre-exponential factor, $E_a$ is the activation energy and k is the Boltzmann constant.

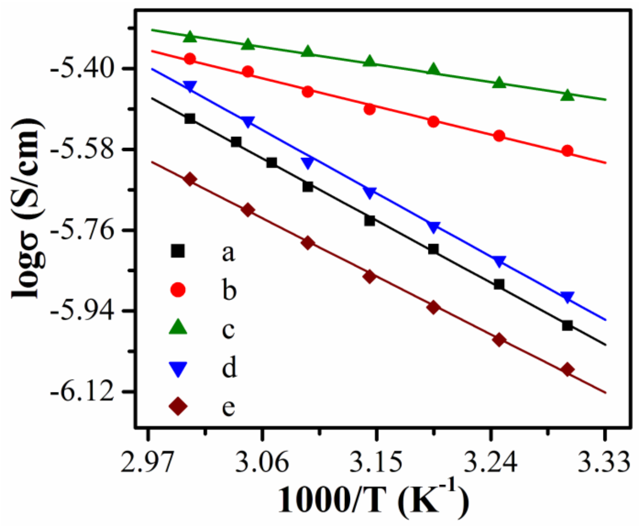

**Fig. 4**. Temperature dependent conductivity of 85PEG-15Mg$(CH_3COO)_2$-x wt% of $Al_2O_3$ CPEs a) 0 wt%, b) 5 wt%, c) 10 wt%, d) 15 wt% and e) 20 wt%.

The behavior of conductivity enhancement with temperature can be understood in terms of the free-volume model **[28]**. As the temperature increases, the polymer can expand easily and produce free volume. Thus, as temperature increases, the free volume increases. The resulting conductivity, represented by the overall mobility of ions and the polymer, is determined by the free volume around the polymer chains. Therefore, as temperature increases, ions, solvated molecules, or polymer segments can move into the free volume. This leads to an increase in ion mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds. The activation energy values calculated from Arrhenius plot are shown in **Table 2**.

*Transport number studies*

The ionic transference number of the mobile species in the polymer electrolyte was calculated by Wagner's dc polarization technique **[20]**. 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/(PEG-$Mg(CH_3COO)_2$-$Al_2O_3$) (85-15-10)/C is shown in **Fig. 5**. The current decays immediately and asymptotically approaches steady state. The total ionic transference number was calculated from the polarization current vs time plots using the standard formula $t_{ion} = (I_i - I_f)/I_i$, where $I_i$ is the initial current and $I_f$ is the final residual current. The total ionic transference number was found to be ~ 0.97 in this polymer electrolyte system. This suggests that the charge transport in these polymer electrolytes is predominantly due to ions.

*Battery discharge studies*

The discharge characteristics of the cell Mg/(PEG-$Mg(CH_3COO)_2$-$Al_2O_3$) (85-15-10)/($I_2$+C+ electrolyte) at an ambient temperature for a constant load of 100 kΩ are shown in **Fig. 6**. The initial sharp decrease in voltage of these cells may be due to polarization and/or formation of a thin layer of magnesium salt at the electrode-electrolyte interface. Various cell parameters obtained for the cell are: cell weight = 1.83 g, area of the cell = 1.33 $cm^2$, open circuit voltage (OCV) = 1.85 V, discharge time for plateau region = 93 h, current density = 13.91 $\mu A/cm^2$, discharge capacity = 1.721 mA h, power density = 13.14 mW/kg and energy density = 1.84 W h/kg.

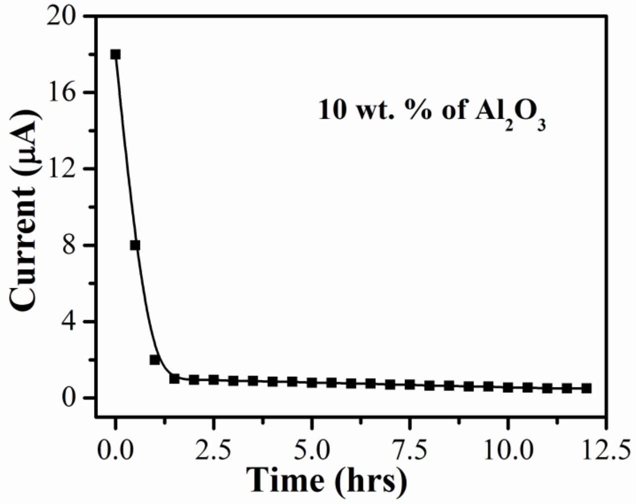

**Fig. 5.** Polarization current vs. time plot of (PEG-$Mg(CH_3COO)_2$-$Al_2O_3$) (85-15-10) electrolyte film.

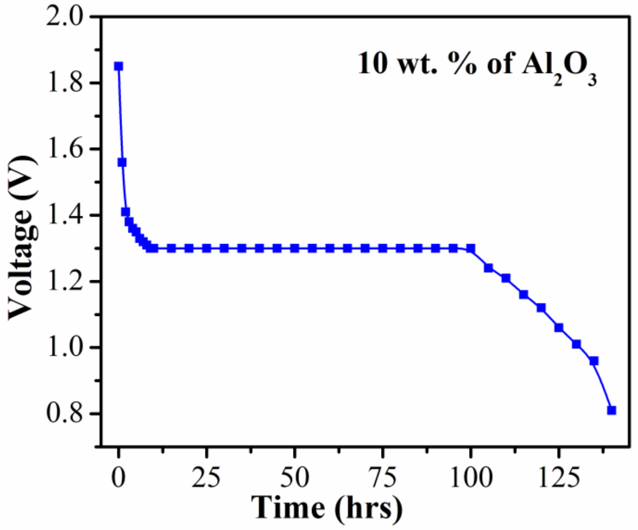

**Fig. 6**. Discharge characteristic plot of (PEG-$Mg(CH_3COO)_2$-$Al_2O_3$) (85-15-10) electrochemical cell for a constant load of 100 kΩ.

## Conclusion

On the basis of experimental investigations on PEG-$Mg(CH_3COO)_2$-$Al_2O_3$ polymer electrolytes, the following conclusions are drawn: 1) Reduction in crystallinity and interaction with the polymer are established from the XRD results after addition of $Al_2O_3$. 2) A decrease in melting temperature and percentage of crystallinity were observed on doping with filler in the SPE. 3) The maximum value of conductivity obtained is $3.45 \times 10^{-6}$ $Scm^{-1}$ for sample with a 10 wt% of $Al_2O_3$ to PEG-$Mg(CH_3COO)_2$ polymer electrolyte system. 4) The ionic transport number data in the PEG-$Mg(CH_3COO)_2$-$Al_2O_3$ polymeric electrolyte films indicate that the conduction is predominantly due to ions. 5) The cell parameters evaluated for the present cell suggest that the present electrolyte system is a worthy candidate for solid state battery application.

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