Ion-Conducting Polymer Electrolyte Based on Poly (Ethylene Glycol) Complexed with $\text{Mg}(\text{CH}_3\text{COO})_2$ - Application as an Electrochemical Cell

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Abstract: A new Mg^{2+} -ion conducting polymer electrolyte based on Poly (ethylene glycol) complexed with $\text{Mg}(\text{CH}_3\text{COO})_2$ has been prepared using solution-cast technique. DSC, Composition-dependent conductivity at different temperatures, dielectric studies, and transference number measurements have been performed to characterize the polymer electrolytes. The DSC measurements show decrease in melting point with increase in salt concentration. Out of five different compositions studied, the 85PEG: 15 $\text{Mg}(\text{CH}_3\text{COO})_2$ polymer-salt complex showed the highest conductivity with $\sigma = 1.07 \times 10^{-6}$ S/cm at room temperature (30°C). The transport number measurements have shown that the electrolyte is an ionic conductor. Using the electrolyte, an electrochemical cell with the configuration $\text{Mg}/(\text{PEG}+\text{Mg}(\text{CH}_3\text{COO})_2)/(\text{I}_2+\text{C}+\text{electrolyte})$ has been fabricated and its discharge characteristics studied.

Keywords: PEG, Polymer electrolytes, DSC, Ionic conductivity, Electrochemical cell.

Introduction

There has been an increasing in the development of solid polymer electrolytes due to their potential applications in solid state electrochemical devices, particularly in solid state rechargeable batteries¹⁻⁷. Compared to liquid based electrolytes, SPEs offer flexibility in shape and size, thus showing a huge potential in miniaturization of battery technology. The ultimate goal in the development of SPEs is to allow high performance operation with a high specific energy density. Among the polymer systems reported, high molecular weight polymer Poly (ethylene oxide)(PEO) is the most widely studied in terms of its complication behavior with several metal salts^{8,9}. Little attention has been paid to the somewhat low molecular weight polymer like poly (ethylene glycol) (PEG) (~ mol. wt. 4000) with metal salts.

Many solid polymeric electrolytes are focused mainly on alkali metal salt systems¹⁰⁻¹⁶, with particular attention given to lithium. Few reports are also appeared on silver and divalent ion conducting polymer electrolytes¹⁷⁻²⁰. However, less attention has been given to SPEs based on magnesium complex systems. Magnesium salts are of considerable interest

because of the divalent charge and the 2:1 anion to cation ratio. It is expected that divalent species with stronger coulomb interaction bears stronger structural and bonding implications in the formation of solid polymer electrolyte and appears as an attractive candidate.

The present work is concerned with solid-state electrochemical cells which are based on (PEG: $\text{Mg}(\text{CH}_3\text{COO})_2$) electrolyte films. Several experimental techniques such as Differential scanning calorimetry (DSC), composition-dependent conductivity at different temperatures and transference number measurements are employed to characterize this polymer electrolyte system. Various cell parameters are reported.

Experimental

PEG (average molecular weight 4,000) purchased from CDH, India, was dried at 40°C for 5 h; $\text{Mg}(\text{CH}_3\text{COO})_2$ (CDH, India) was dried at 40°C for 24 h. Solid polymer electrolyte samples were prepared using the solution cast technique. PEG (molecular weight of 4,000) was used as the polymer. $\text{Mg}(\text{CH}_3\text{COO})_2$ 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. 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 a desiccator for further drying before the test.

The thermal response was studied by Differential Scanning Calorimetry (TA Instruments mod. 2920 calorimeter) in the static nitrogen atmosphere at a heating rate of 5°C/min. in the temperature range 0 to 100°C. Conductivity measurements were carried out using a HIOKI 3532-50 impedance analyzer in the frequency range 50 Hz to 1 MHz. The transference number measurements were made using Wagner's polarization technique²¹. Using the polymer electrolyte films, solid-state electrochemical cells have been fabricated with the configuration $\text{Mg}/(\text{PEG}+\text{Mg}(\text{CH}_3\text{COO})_2)/(\text{I}_2+\text{C}+\text{electrolyte})$ under a constant load of 100 k Ω .

Results and Discussion

The differential scanning calorimetry (DSC) curves of pure PEG and different composition of PEG: $\text{Mg}(\text{CH}_3\text{COO})_2$ polymer electrolyte are given in Figure 1.

Figure 1. DSC curves of different compositions of PEG: $\text{Mg}(\text{CH}_3\text{COO})_2$ solid polymer electrolyte.

The melting temperature (T_m) of PEG based polymer electrolytes are decreased with increase of $Mg(CH_3COO)_2$. The T_m values of PEG based polymer electrolytes are given in Table 1. The low melting point is observed for optimum conducting composition; this is in good agreement with conductivity results²². In addition, the melting endotherm is found to broadened with increase of salt concentration. The decreasing in the melting temperature and broadening of the melting endotherm are clear indications of decrease in the degree of crystallinity and dominant presence of amorphous phase.

Table 1. Melting point (T_m) values of PEG: $Mg(CH_3COO)_2$ polymer electrolytes.

Sample	Melting point (T_m) (in °C)
100:0	59.42
90:10	57.65
85:15	55.32
75:25	56.57

The ionic conductivity of polymer electrolytes as a function of magnesium acetate concentration at various temperatures is shown in Figure 2.

Figure 2. Variation of logarithmic conductivity as a function of $Mg(CH_3COO)_2$ concentration for various temperatures.

The conductivity of pure PEG was 5.41×10^{-8} S/cm at 303 K and its value increased to 1.07×10^{-6} S/cm on complexing²² it with 15% of $Mg(CH_3COO)_2$. For all compositions of the PEG with $Mg(CH_3COO)_2$ salt, the conductivity increases with increase of temperature. This may be explained on the basis of an increase in either ionic mobility or the concentration of carrier ions [23]. The ionic conductivity values are given in Table 2.

In general, it is believed that the conductivity increases as the degree of crystallinity decreases or, in other words, as the flexibility of the polymeric backbone increases. The observed continuous increase in conductivity of the (PEG: $Mg(CH_3COO)_2$) system with increasing salt concentration is attributed to a decrease in the degree of crystallinity, as confirmed by DSC analysis.

Table 2. Ionic conductivity values of PEG: Mg(CH₃COO)₂ polymer electrolytes at various temperatures.

Sample	Ionic conductivity, S/cm			
	303 K	313 K	323 K	333 K
100:0	5.41E-08	1.07E-07	2.05E-07	4.6E-07
95:05	4.23E-07	5.91E-07	9.18E-07	1.32E-06
90:10	3.33E-07	4.53E-07	7.47E-07	1.08E-06
85:15	1.07E-06	1.58E-06	2.07E-06	3.38E-06
75:25	9.21E-07	1.15E-06	1.64E-06	3.11E-06

The complex permittivity ϵ^* of a system is defined by $\epsilon^* = \epsilon' - j\epsilon'' = \epsilon' - j(\sigma'/\omega\epsilon_0)$. Where ϵ' is the real part (dielectric constant) of complex permittivity, ϵ'' is the imaginary part (dielectric loss) of dielectric permittivity, σ' is the real part of conductivity, ω is the angular frequency and ϵ_0 is the permittivity of the free space.

The frequency dependent imaginary part of dielectric permittivity for different compositions at 303 K and for 85PEG: 15Mg(CH₃COO)₂ polymer complex at different temperatures are shown in Figures 3(a) and 3(b) respectively.

Figure 3. Variation of ϵ'' with $\log\omega$ for PEG:Mg(CH₃COO)₂ system (a) at different salt concentrations, (b) at different temperatures for optimum composition (85:15).

At low frequencies, the value of ϵ'' is high which can be explained by the presence of space charge effects which is contributed by the accumulation of charge carriers near the electrodes^{24,25}. As the frequency increases, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases leading to the decrease in the value of ϵ'' . From Figure 3(a), the higher value of ϵ'' has been observed for the polymer electrolyte containing 15 wt % of Mg(CH₃COO)₂ at 303 K. This may be due to enhanced charge carrier density at the space charge accumulation region resulting in an increase in the equivalent capacitance.

As the temperature increases, the value of ϵ'' of the polymer electrolyte increases. Since there is no appreciable relaxation peaks observed in Figure 3(b). The dielectric constant in the present study has been used to show that the increase in conductivity is mainly due to the increase in the number density of mobile ions²⁶.

Figure 4 shows the variation of current as a function of time upon the application of a DC voltage of 1.5 V across the cell $\text{Mg}/(\text{PEG}+\text{Mg}(\text{CH}_3\text{COO})_2)/\text{C}$. The transference number has been calculated which is found to be $t_{\text{ion}} = 0.96$. This suggests that the charge transport in these polymer electrolyte films is predominantly due to ions.

Figure 5 shows the discharge characteristics of the electrochemical cell $\text{Mg}/(\text{PEG}+\text{Mg}(\text{CH}_3\text{COO})_2)/(\text{I}_2+\text{C}+\text{electrolyte})$ for a constant load of 100 k Ω . 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 3.

Figure 4. Current versus time plot of $\text{PEG}:\text{Mg}(\text{CH}_3\text{COO})_2$ (85:15).

Figure 5. Discharge characteristics of $\text{PEG}:\text{Mg}(\text{CH}_3\text{COO})_2$ (85:15) electrochemical cell (load = 100 k Ω).

Table 3. Cell parameters of $[\text{PEG}+\text{Mg}(\text{CH}_3\text{COO})_2]$ electrolyte cell at a constant load of 100 k Ω .

Cell Parameters	$\text{Mg}/[\text{PEG}+\text{Mg}(\text{CH}_3\text{COO})_2](80:20)/(\text{I}_2+\text{C}+\text{electrolyte})$
Cell weight	1.8 g
Area of the cell	1.33 cm ²
Open circuit voltage (OCV)	1.84 V
Discharge time for plateau region	82 h
Current density	13.84 $\mu\text{A}/\text{cm}^2$
Discharge capacity	1.51 m A h
Power density	12.93 mW/Kg
Energy density	1681 mW h/Kg

Conclusion

The DSC measurements of PEG with $\text{Mg}(\text{CH}_3\text{COO})_2$ salt showed a decrease in the degree of crystallinity and increase of amorphous regions with increasing concentration of the salt. The conductivity studies indicate that the ionic conductivity of pure PEG and $(\text{PEG}+\text{Mg}(\text{CH}_3\text{COO})_2)$ films increased with increasing temperature and dopant

concentration. Transference number data shows that the conductivity is mainly due to ions. The electrochemical cell results show that (PEG+ Mg(CH₃COO)₂) system is a potential candidate for fabrication of solid state batteries.

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