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Effect of plasticizer on electric and dielectric properties of PVA-$MgBr_2$ based solid polymer electrolytes.

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Abstract

This paper report the synthesis and properties of a series of composite polymer electrolytes formed by dispersion of tetraethylene glycol dimethyl ether (TEGDME) into poly (vinyl alcohol) complexed with magnesium salt. Scanning electron microscope (SEM) images of different TEGDME concentrations of films revealed that TEGDME dissocit the agglomeration of salt and some pores appers at the surface. The addition of TEGDME greatly enhances ionic conductivities of the electrolytes which is due to the high polarity and diffusivity of TEGDME. The optimum ionic conductivity value of the plasticized polymer electrolyte film of 1 wt.% TEGDME has been achieved to be of the order of 10^{-6} S.cm^{-1} at room temperature. Dielectric properties have been studied for different wt.% of plasticizer and their variations have been observed.

1. Introduction

Solid polymer electrolytes (SPE) have been widely studied due to their applicability for a variety of solid state and electrochemical device applications including batteries, fuel cells, super capacitors, electro chromic devices and chemical sensors [1]. Studies the electrical properties of polymer electrolyte are more important in view of these applications [2], because it aiming to understand the nature of the charge transport in these materials. Also the dielectric constant and dissipation factor (as a function of temperature or frequency) are very important in the design of devices and gives us more information on the chemical or physical state of the polymer [3].

The electrical and dielectric properties of polymer can be modified by addition of dopants [2]. PVA is polymer showing excellent properties such as a very high dielectric properties, good charge storage capacity and dopant-dependent electrical and optical properties [4]. It has carbon chain backbone with hydroxyl groups attached to methane carbons; these OH groups can be a source of hydrogen bonding and hence assist the formation of polymer electrolytes [4].

When salts dissolve in a polymer matrix, it is produce ions which serve as charge carriers that contribute to ionic conductivity under the influence of an electric field. Usually, chosen of the salt based on the size of the anions, e.g., $LiClO_4$, NaBr or LiH_2PO_4 [5], but in this work, $MgBr_2$ salt is the doping salt.

Various approaches such as addition of fillers, blending, plasticization..etc. have been made to enhance the conductivity of polymer electrolytes [1]. The most important advances in increasing the conductivity of solid polymer electrolytes by added of suitable amounts of plasticizers [1], because the high dielectric constant plasticizers able to dissociate the ion-pairs into free cations and anions which lead to increase in the conductivity [6]. TEGDME was chosen due to it is good properties, such as the high boiling point and low volatility, which make it a good choice as electrolyte of batteries [7].

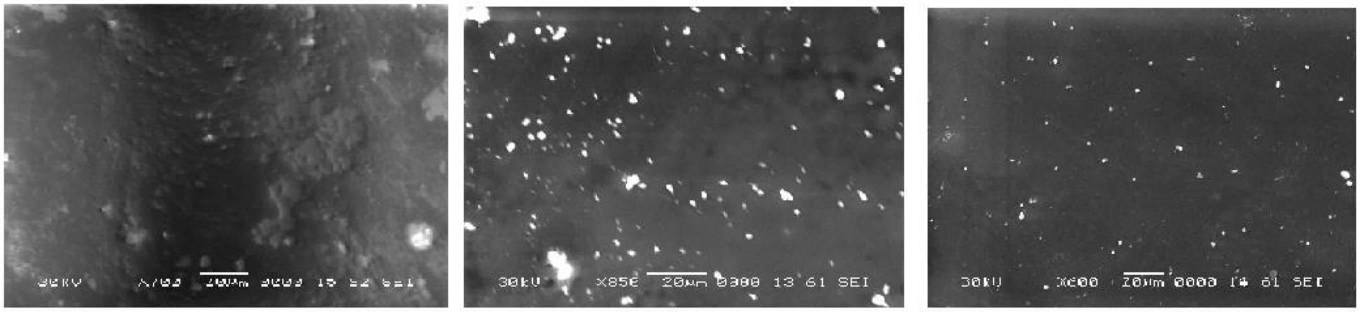

Fig 1: The SEM micrograph for the surface of $PVA_{0.7}(MgBr_2)_{0.3}/_xTEGDME$ SPE

Upon the above considerations, an attempt has been made to characterize the solid polymer electrolytes based PVA-$MgBr_2$ and TEGDME at different weight percentages of TEGDME to evaluate their physio-chemical performance.

2. Experimental section

All chemicals used in the present study received from Sigma Chemical Company, Germany. To synthesis $(PVA)_{0.7}(MgBr_2)_{0.3}$ membrane, 0.3 wt.% magnesium bromide ($MgBr_2$) were added to 0.7 wt.% PVA $(C_2H_4O)_n$ (98–99% hydrolyzed, average MW 88000–97000) and stirred using a magnetic stirrer at 60 ^oC for 10 hrs. The prepared solution was direct cast in a petri-glass dish and left for ten days at dry atmosphere.

To synthesis $(PVA)_{(0.7)}(MgBr_2)_{0.3}/_xTEGDME$ membrane, TEGDME with different concentrations, x = 0, 0.2, 0.4, 0.6, 0.8 and 1 ml was added to $(PVA)_{0.7}(MgBr_2)_{0.3}$ and stirred using a magnetic stirrer at 60 ^oC for 10 hrs. The prepared solutions were direct cast in a petri-glass dishes and left for ten days at dry atmosphere.

For measuring the DC conductivity, the samples were prepared with diameter 0.5 cm. The two parallel surfaces of the sample were given a coating of silver using conducting silver paint and sandwiched between the two similar stainless steel electrodes of a spring-loaded sample holder. The samples were heated from room temperature at a rate 2 ^oC/min in an electric furnace with winding run in opposite directions to eliminate the fields due to the heating current.

The electrodes were connected to the measuring instrument using two shielded cables. The direct current, I, was measured by a Kithely 485 programmable electrometer.

Dielectric properties of the samples were performed in the temperature range 303–423 K over the frequency range 100 Hz–100 KHz using PM 6304 programmable RCL (Philips) meter.

3. Results and discussion

Depending on the type and amount of TEGDME in the polymer matrix, the morphology of the polymer electrolyte will vary and greatly influence its properties. Morphological examination of this study is carried out to study the phase morphology changes of the pure and the resulting plasticized Mg salt solid polymer-electrolyte. Scanning electron micrographs of untreated and TEGDME doped have been presented in Fig. 1.Very distinguishable changes can be observed from SPE and high concentrations of TEGDME doped SPE. Pure SPE shows some agglomeration of salt at the surface. The morphology changes, as soon as TEGDME is incorporated into the polymer. The morphology changes drastically to become significantly more smooth also the agglomeration of salt dissociate and some pores observed at the surface. This porous structure provides enough channels for the migration of ions, accounting for better ionic conductivity [8].

Fig.2 shows the dc conductivity of $PVA_{0.7}(MgBr_2)_{0.3}/_xTEGDME$ SPE as a function of TEGDME content. The highest conductivity of $PVA_{0.7}$ $(MgBr_2)_{0.3}/_{x'}TEGDME$ polymer electrolyte film is 1.3 x 10^{-6} $S.cm^{-1}$ when 1wt.% TEGDME was added. TEGDME increases the dissociation of salt and thereby produces more free ions which increases the conductivity. Also, the ability of the plasticizer to penetrate the polymer matrix and establish attractive forces/reduce the cohesive forces between the polymer chains increases the segmental mobility, which enhances the conductivity of polymer electrolyte [1].

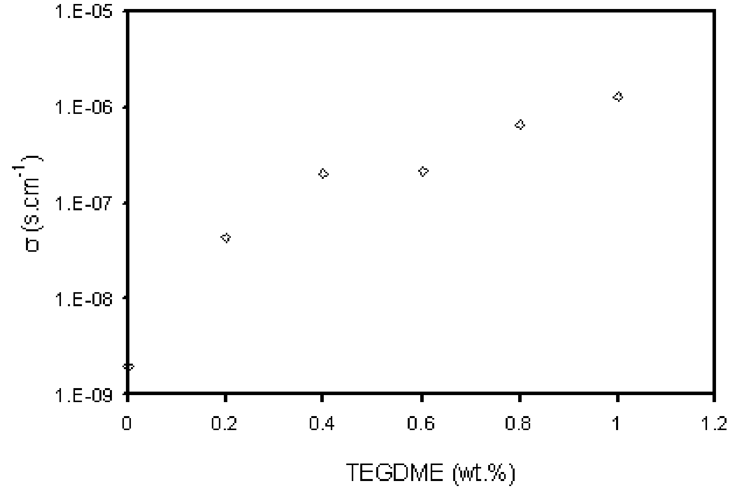

Fig 2: DC conductivity of $PVA_{(0.7)}(MgBr_2)_{0.3}/_x$TEGDME SPE against TEGDME concentration.

Fig.3 shows the temperature - dependent ionic conductivity of $PVA_{0.7}(MgBr_2)_{0.3}/_x$TEGDME SPE. From the plot, it is evident that, as temperature increases the conductivity also increases. The increase in conductivity with temperature has been explained in terms of segmental motion that result in increasing free volumes of the sample and the motion of ionic charge. The conductivity can be expressed as [6].

$$\sigma = \sigma_0 \exp^{(-E_a/KT)} \qquad (1)$$

where σ_0 is the pre-exponential factor, E_a is the energy of activation for conduction, K_B is Boltzmann constant and T is the temperature in Kelvin. As shown in Fig.3. Activation energy at different concentrations of TEGDME was obtained using fitting of Eq.1. Table 1 presents the activation energy data; it can be observed that the lowest activation energy is for the film doped with 1 wt.% TEGDME, which indicate that TEGDME have effect on Mg $^{2+}$Br$^-$ dissociation and ionic transfer.

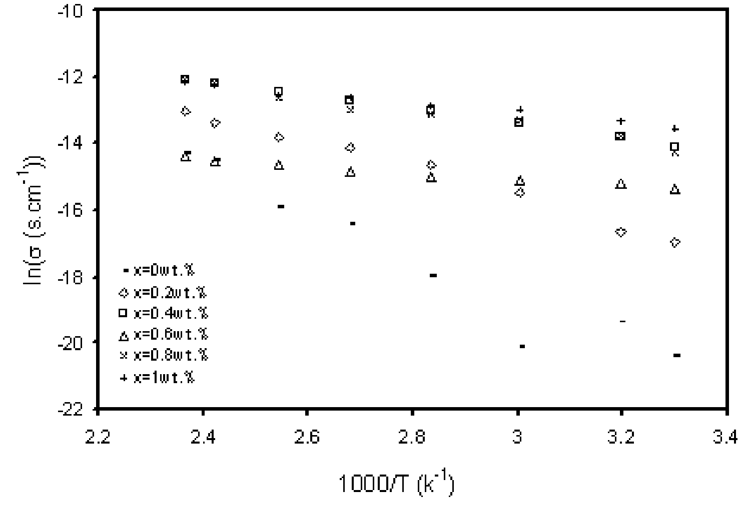

Fig 3: Temperature dependence of the dc electrical conductivity for $PVA_{(0.7)}(MgBr_2)_{0.3}$ $/_x$TEGDME SPE.

Table 1: The calculated values of E_a (eV), E_h(eV), T_o and $N(E_f)$ for $PVA_{0.7}(MgBr_2)_{0.3}/_x$TEGDME SPE.

x wt.%	**E_a(eV)**	**E_h (eV)**	**$N(E_f)$ x10^{19} (cm^{-3}/eV)**	**T_o x10^7 (K)**
0	0.52	0.53	0.69	3.11
0.2	0.36	0.37	1.26	1.69
0.4	0.18	0.18	2.10	1.02
0.6	0.08	0.11	1.20	1.77
0.8	0.18	0.19	2.06	1.03
1	0.12	0.13	2.22	0.96

The σ_{dc}-T relation can be analyzed by applying another model, which namely the Mott model in which the electrical conductivity follows the relation [9-10],

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_o}{T}\right)\right]^{1/4} \qquad (2)$$

Where σ_o is a moderately temperature-dependent pre-exponential factor and T_o is the characteristic temperature that determines the thermally activated hopping among localized states at different energies which considered as a measure of disorder and given by [11-13],

$$T_o = \lambda\alpha^3 / k_B N(E_f) \qquad (3)$$

Where λ=18.1 is a dimensionless constant, α^{-1}=10 A^o is decay length of the wave function and $N(E_f)$ is the density of state at the Fermi level. Both the temperature parameter, T_o, and the density of states $N(E_f)$ for all investigated samples were calculated using the least square fitting of equation (2) and (3) and also listed in table (1). The decrease in T_o with increasing the salt content as shown in this table is attributed to the effect of dispersion and coalescence of all additions with the polymer. The marked increase in $N(E_f)$ with decreasing of T_o for all samples indicate that the conducting paths change the geometrical characteristics (i.e. interchain distance among conductive sites) inside the polymer matrix with increasing plasticizer content [14-15].

In order to elucidate the type of conduction mechanism in all samples, the logarithmic plots between σ_T versus 1/T were studied according to the formula [16],

$$\sigma\sqrt{T} = A\exp-\left(E_h / k_B T\right) \qquad (4)$$

Where A is constant and E_h is an activation energy for charge carrier hopping. This relation confirms our expectation that the conduction mechanism in all samples is attributed to hopping one. The estimated values of E_h as a function of plasticizer content for samples are listed in table (1).

Fig.4 illustrates the variations of the dielectric permitivity ε' of $(PVA)_{0.7}(MgBr_2)_{0.3}/_x$TEGDME SPE versus frequency at different content of TEGDME. From this figure, one can noticed that, ε' decrease gradually with increasing frequency for all prepared samples. This behavior can be described by the Debye dispersion relations [17]:

$$\varepsilon' \cong \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1+\omega^2\tau^2} \qquad (4)$$

Where ε'_∞ and ε'_s are the infinite and static dielectric permittivities respectivly, τ is the dielectric relaxation time and ω is the angular frequency. The decrease of ε' with frequency can be associated to the inability of dipoles to rotate rapidly leading to a lag between frequency of oscillating dipole and that of applied field [4].

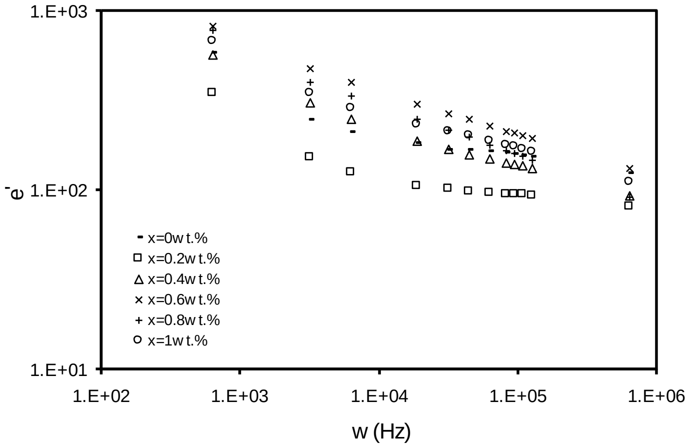

Fig 4: Dependence of dielectric constant on frequency at room temperature for $PVA_{0.7}(MgBr_2)_{0.3}/_x$TEGDME SPE.

Fig.5 shows the variation of the dielectric constant ε' of $(PVA)_{0.7}(MgBr_2)_{0.3}/_x$TEGDME SPE versus temperature T, at constant frequency,1 kHz. The dielectric constant increased with increasing temperatures. The increase of ε' with temperture due to the orientation is facilitated as the temperature increases.

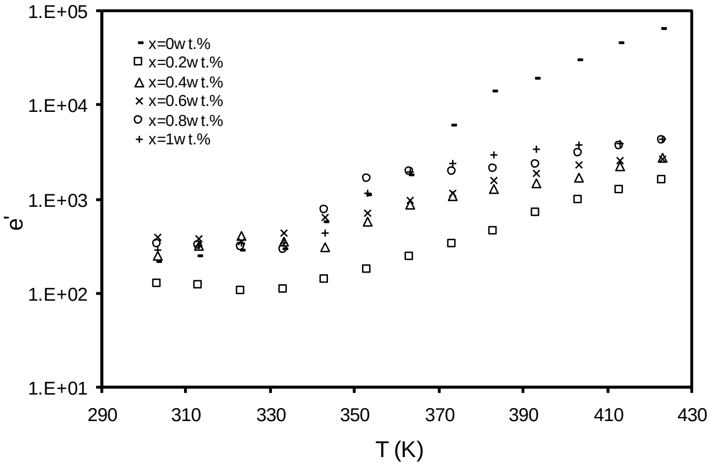

Fig 5: Dependence of dielectric constant on temperture at 1 kHz for $PVA_{0.7}(MgBr_2)_{0.3}/_x$TEGDME SPE.

4. Conclusion

The approach of combining a polymer, slat and plasticizer to generate a new type of magnesium ion conductor have been succeded. The result can summarized as follow:

1. Addition of TEGDME enhanced the morphology of the surface.
2. The addition of TEGDME increases the dissociation of salt and thereby produces more free ions which increases the conductivity.
3. The ionic conductivity depended on the content of TEGDME. The highest conductivity of the SPE examined was 1.3 x 10^{-6} S. cm^{-1} (at room temperture) for the composition of 1 wt.% TEGDME.
4. Dielectric constant decrease with increasing frequency and increased with increasing temperature.

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