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RESEARCH ARTICLE

INFLUENCE OF Al_2O_3 NANOPARTICLES ON STRUCTURAL AND ELECTRICAL PROPERTIES OF PVP-MgBr₂ POLYMER ELECTROLYTE FILMS

Moses. V. G. Isaiah¹, Mangalam, G. ^{2,*} and Hamsavalli, G.¹

¹Department of Physics, Velammal Engineering College, Chennai-600066, India

²PG and Research Department of Physics, Pachaiyappa's College, Chennai-600036, India

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*Corresponding Author:

Mangalam, G.

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ABSTRACT

In this present study, nanocomposite polymer films are prepared based on PVP and MgBr₂ with doping of additive plasticizers (Al_2O_3) with different ratios using solution cast technique. XRD pattern confirms the semi crystalline nature of the polymer films. The ionic conductivity of the prepared films was measured by using AC impedance spectroscopy and it is found to be at 10^{-2} S/cm. The electrical conductivity studies were carried out by DC ionic conductivity set up and for the composition of 85 (PVP):15(MgBr₂):0.1(Al_2O_3), the highest ionic conductivity was found to be at 1.25×10^{-2} S/cm at room temperature. The conductivity is found to increase with increase in temperature. The temperature dependent conductivity of the polymer electrolyte follows the Arrhenius relationship which shows hopping of ion mechanism in the polymer matrix.

INTRODUCTION

From the past few decades, researchers and scientists draw their attention towards the advancement of nano composite polymer electrolytes (NCPE) and widely studied for many applications like sensors, solid state batteries and fuel cells (Guo, 2010; Zhang, 2011). Ongoing investigations have been found that NCPE particle directing frameworks for their possible use in strong state batteries with the high cell voltages and energy densities that are normal for rechargeable batteries. A great deal of exploratory examination has been made on monovalent salt frameworks like Magnesium salts (Li, 2013); little consideration has been given to the polymer electrolytes in which multivalent cations are the portable species. Magnesium metal has various qualities that make it appealing as a negative cathode material for battery-powered batteries, including its minimal expense, relative plentitude, high conductivity, non toxic which takes into account metropolitan garbage removal (Lin, 2013). Considering insignificant perils and upgraded wellbeing, examines of battery-powered magnesium batteries are relied upon to have a wide extension in the future (Gao, 2011; Abdelrazek, 2010; Stoller, 2008; Yuvi 2009; Stankovich 2007).

There have been a few examinations on the strong polymer electrolytes dependent on magnesium salts (Stankovich, 2007; Fu, 2015). An option in contrast to the utilization of monomer cations is to utilize polycations to make another Al^{+} particle leading strong polymer electrolyte framework. This adjustment might prompt improved material properties like adaptability, grip, and thermally stable in an ionically conductive polymer sheet. The core mechanism of conductivity lies behind, as far the doping of additive nano filler to the host matrix the transport of ions increases abruptly. Therefore, some of the investigations have been performed with other metal particle directing polymers like Aluminium oxide and just a set number of aluminium particles leading polymer electrolyte frameworks have been contemplated (Eda, 2009; Okada, 2006). The NCPs display high conductivities up to 10^{-2} S/cm at 373 K (Kojima, 1993). Polymer salt complex with high ionic conductivity have been widely explored in the course of recent a long time because of their likely applications as electrolyte material in high-energy-thickness strong state batteries (Thutupalli, 1976). The polymer battery enjoys the benefit of having high-energy thickness, dissolvable free condition, non rust condition and light weight. Polyvinylpyrrolidone (PVP) has drawn an extraordinary consideration among the formed polymers due to

PVP is a potential material having a good charge storage capacity, electrical and optical properties. Artificially PVP has will undoubtedly be latent, nontoxic and it shows a solid propensity for complex development with a wide assortment of nano particles. In the current examination, magnesium bromide complexed with PVP polymer electrolytes with additive plasticizers of Al_2O_3 films were prepared and contemplated.

Experimental details

PVP with average molecular weight (M.W: 36,000) and magnesium bromide ($MgBr_2$) with 98% pure and Al_2O_3 Nano filler 99% pure were purchased from Sigma Aldrich chemicals, India. The samples were prepared by properly measured the different wt% ratios and distilled water is used as a solvent in this process. The above mentioned chemicals were allowed to continuous stirring for 24 h in a conical flask for complete dissolution. After the obtained homogenous solution was casted in polypropylene petri-dishes and kept in a hot air oven at $60^\circ C$ for 48 h to evaporate the solvent. A set of nano composite PVP- $MgBr_2$ - Al_2O_3 polymer electrolyte films were prepared at different wt% ratios (95:5:0.1), (90:10:0.1) and (85:15:0.1). Finally the obtained films were kept in desiccators until further characterization. X-ray diffraction studies were performed by using a Philips analytical X'pert diffract meter in the diffraction 2θ angular range 10 - 90° with nickel filtered $CuK\alpha$ radiation ($\lambda=1.5403 \text{ \AA}$). The dielectric and impedance measurements of the prepared films were carried out in the frequency between 5000 and 50000 Hz on HIOKI 3532-50 LCR Heister.

RESULTS AND DISCUSSION

XRD Analysis: X-ray diffraction design is fundamental to get the crystalline structural information on the given material. Under the investigation if the sample seems to be crystalline then it tends to be well defined peaks. While non-crystalline or amorphous systems show a broad peaks rather than well defined peaks (Kuilla, 2010; Morimun, 2011). The X-ray diffraction sample of pure PVP and PVP complexed with $MgBr_2$ with the addition of nano filler Al_2O_3 were displayed in Figure 1.

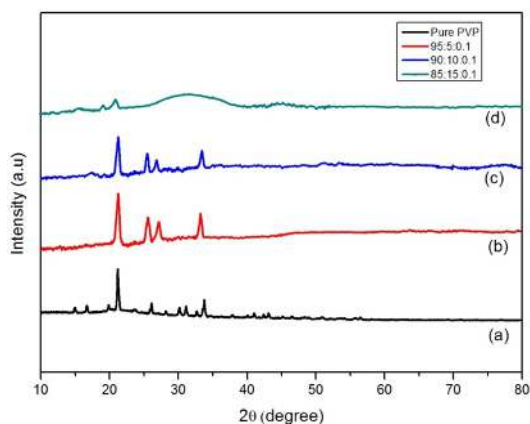


Fig. 1. XRD pattern of NCPs films (a) Pure PVP (b) PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1) (c)PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1) (d) PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1)

In the figure, the Pure PVP shows sharp peaks at an angle of $2\theta= 21.8, 26.23, 30.33, 31.11, 33.63^\circ$ this indicates the sample

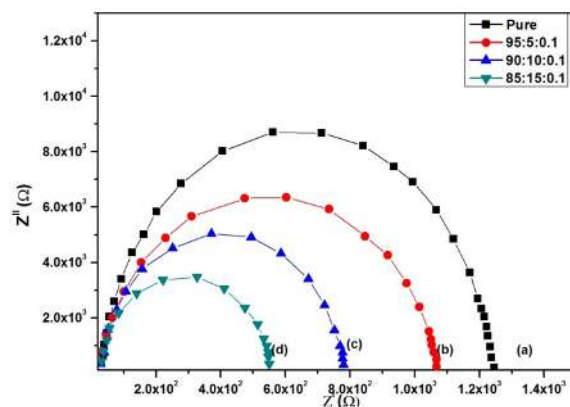


Fig. 2. Impedance plots of NCPs films (a) Pure PVP (b) PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1) (c)PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1) (d) PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1)

The intensity of these peaks step by step diminishes with the increment of $MgBr_2$ along with additive nano filler Al_2O_3 . This could be because of the interruption of the PVP glass like structure by $MgBr_2$. From the figure it is observed that the XRD peaks for the compositional ratios of (PVP+ $MgBr_2:Al_2O_3$) (95:5:0.1, 90:10:0.1) are found to be at $2\theta=21.34, 25.47, 27.05, 33, 19^\circ$.

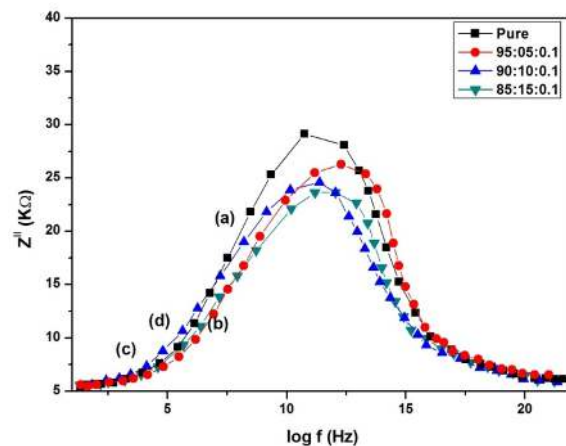


Fig. 3 $\log f$ vs ϵ'' of NCPs films (a) Pure PVP (b)PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1) (c)PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1) (d) PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1)

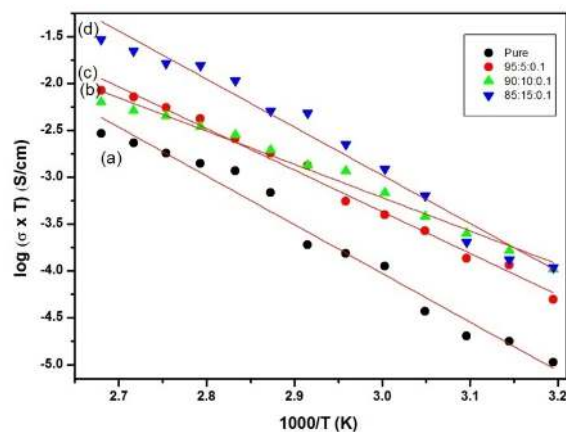


Fig. 4 DC conductivity of NCPs films (a) Pure PVP (b) PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1) (c)PVP+ $MgBr_2:Al_2O_3$ (95:05:0.1) (d)

Table.1. DC conductivity values of PVP+ MgBr₂:Al₂O₃ nanocomposite polymer films

Nanocomposite polymer films	Conductivity values at 373 K (Scm ⁻¹)	Conductivity values at 373 K (Scm ⁻¹)
Pure PVP	1.93 x 10 ⁻⁶	2.21 x 10 ⁻⁴
PVP+ MgBr ₂ :Al ₂ O ₃ (95:05:0.1)	2.54 x 10 ⁻⁵	1.61 x 10 ⁻³
PVP+ MgBr ₂ :Al ₂ O ₃ (90:10:0.1)	3.29 x 10 ⁻⁴	1.59 x 10 ⁻²
PVP+ MgBr ₂ :Al ₂ O ₃ (85:05:0.1)	2.01 x 10 ⁻³	1.23 x 10 ⁻²

This shows a diminishing in the level of crystallinity of polymer after the expansion of salt. It is observed that; at high compositional ration (85:15:0.1) the intensity of the peaks are quietly decreases. No other sharp peaks were noticed for higher groupings, this indicates the complete dissolution of salt within the host polymer the additional peaks which are observed at 33.19⁰ and 33.63⁰ may be due to the addition of nano filler in the host polymer. This recommending the dominant presence of amorphous phase.

Complex impedance examination: AC impedance spectroscopy is a powerful technique which is used to measure the electrical properties of the material. The impedance (Cole–Cole) plots of PVP doped MgBr₂ for the different compositions of the films with additive nano filler 0.1(Al₂O₃) fixations are displayed in Figure 2. The plot comprises of a high frequency semicircle which might be because of the mass impact of the electrode-electrolyte interfaces. The block of the half circle or spike with the genuine impedance (Z') pivot gives the mass electrical obstruction (R_b) of the polymer electrolytes. The ionic conductivity (σ) of the polymer electrolytes has been determined by using the following equation

$$\sigma_{ac} = \frac{t}{R_b A} \quad (1)$$

where R_b is the bulk resistance, t is the thickness of the film and A is the cross sectional area of the electrolytes individually. The ionic conductivity esteems for the various compositions of PVP doped MgBr₂ with an additive fillers Al₂O₃ at various temperatures are introduced. More amount of salt added into the polymer matrix leads to increase in the viscosity of the polymer electrolyte films (Tyler, 2006). Consequently, the mobility of the charge carriers has been decreased due to free space and the ion transportation is reduced. Hence, the conductivity is decreased for higher compositions.

The most elevated ionic conductivity at surrounding temperature has been viewed as 2.64×10⁻⁶ to 1.25×10⁻² S/cm for 85 (PVP):15(MgBr₂):0.1(Al₂O₃) nanocomposite polymer electrolyte film. Figure 3 addresses the intricate impedance plot of the greatest conductivity test at surrounding temperatures. The higher dielectric constant at low frequency side is attributed to the addition of nano filler in the polymer matrix which brings a more expansion in charge carriers and consequently conductivity (Khan, 2010). The major role of a plasticizer in a host polymer is to diminish thickness of the electrolyte and aid the separation of the salt; this results in expanding the quantity of charge transporters. The decline in conductivity has been observed at higher grouping, this might be because of the segregation of the ions.

Dielectric properties: The variation of dielectric constant with logerthermic frequency of polymer films for different wt% ratios of PVP doped MgBr₂ with additive fillers Al₂O₃ at room temperature is shown in Figure.3. It is observed from the figure; as increasing the logerthermic frequency, the dielectric constant values are gradually decreases and found to be high for the sample prepared with 85 (PVP):15(MgBr₂):0.1(Al₂O₃), this concludes that the drifting of ions is high giving raise to conductivity phenomenon. It is observed that the dielectric steady and dielectric misfortune increment with increment of logarithmic frequency. This increment builds due to the level of salt separation and dissociation of the particle bringing about the increment in the quantity of free particles or charge transporter thickness (Paredes, 2008).

This reveals that the salt is completely dissolute in the polymer chains giving raise to mobile ions whereas dispersion of nano fillers enhance the charge carriers results in increase of an ionic conductivity. The upsides of ε" are extremely high at low frequencies and somewhat steady at higher frequencies. Such high worth of ε" might be because of the interfacial impacts inside the greater part of the sample due to the formation of space charge region at the electrode and electrolyte interfaces a variation is observed in between dielectric constant of ε". The loss spectra characterized by peak appearing at a characteristic frequency for polymer samples suggest the presence of relaxing dipoles in the samples and also with electrical relaxation process or inability of dipoles (Ping, 2017). It is evident that the peak is shifted towards higher frequency side thereby reducing the relaxation time. This tends in the improvement in charge transporter thickness in the space charge area.

DC ionic conductivity: Conductivity estimations have been made for different wt% ratios of PVP doped MgBr₂ with additive fillers Al₂O₃ at room temperature which is shown in Figure. 4. The determined conductivity from the qualities; it is tracked down that the conductivity increments with expanded temperature just as convergence of salts and the nano fillers (Shahenoor Basha, 2017). It is observed that; the ionic conductivity of the 85 (PVP):15(MgBr₂):0.1(Al₂O₃), proportion is more prominent than on account of other wt% ratios. From Figure 5 i.e., log σT versus 1000/T plot, all blends are straightly fluctuating with temperature. At room temperature, the conductivity of pure PVP has measured up to 1.93 x 10⁻⁶ S/cm and its value increases abruptly up to 2.21x 10⁻⁴ S/cm on increasing the temp at 373K. The ionic conductivity and the temperature shows an Arrhenius sort of thermally initiated process. In these areas, the conductivity is measured by

$$\sigma_{dc} = \frac{iL}{VA} \quad (2)$$

where i is the current, t is the thickness of the film, V is the applied voltage and A is the area of the cross section of the film. Among all the compositional ratios the high ionic conductivity was found up to 1.23 x10⁻² S/cm for the 85(PVP):15(MgBr₂):0.1(Al₂O₃) and other compositional ratios and its ionic conductivity values are listed in Tabel.1. From the figure it is observed clearly; the conductivity values increases sharply as increase in the temperature whereas the dispersion of the nano filler in the electrolyte films enhances the ionic conductivity (Wan, 2014). But further addition of nanocomposites the conductivity may be decreased at a higher

concentration, because of segregations of ions which decreases overall mobility (Lv, 2009). The increase in conductivity with respect to temperature was explained by Arrhenius plots; as the temperature increased the conductivity of the electrolyte films also increased. This favours hopping mechanism between coordinating sides, local structure relaxation and segmental motion of the polymer.

Conclusion

PVP+MgBr₂:Al₂O₃ nanocomposite polymer electrolyte films with different ratios of Al₂O₃ were prepared by solution casting technique. XRD patterns showed the broad diffraction peaks at $2\theta = 21.8, 26.23, 30.33, 31.11, 33.63^\circ$ which attributes the diminishing in the level of crystallinity of polymer after the expansion of salt.

From the impedance plot and DC ionic conductivity values it is observed that; the most elevated ionic conductivity at surrounding temperature has been viewed as 2.64×10^{-6} to 1.25×10^{-2} S/cm for 85 (PVP):15 (MgBr₂):0.1(Al₂O₃) at room temperature. The dielectric steady and dielectric misfortune increases with an increment of logarithmic frequency.

Conflict of Interest: The authors declare that they have no conflict of interest

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