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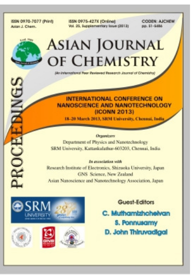

Ionic Conductivity Studies on Nano ZnO Incorporated PVC-PEG Blend Based Polymer Composite Electrolytes†

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Nano-sized ZnO was prepared by sol-gel method and it was incorporated as filler in PVC-PEG blend based solid polymer electrolytes with lithium perchlorate as salt. The (PVC:ZnO) ratio was systematically varied in order to study its effect on the ionic conductivity behaviour of electrolyte membranes. The membranes were subjected to XRD and AC impedance analysis. The analysis shows that the conductivity profile was strongly influenced by the (PVC:ZnO) ratio. The conductivity profile exhibits two maxima one occurring at 0.5 wt % and the other at 4 wt % of filler. The membrane with composition, (PVC:ZnO):PEG:PC:$LiClO_4$ = (21:4):15:50:10 exhibits higher conductivity of 6.052×10^{-6} S/cm at room temperature and this value is 10 times higher than that of filler free electrolytes.

Key Words: Nano ZnO filler, Polymer electrolytes, Xrd studies, Ionic conductivity.

INTRODUCTION

The development of polymer electrolytes has gained a new momentum in the recent years due to the possibility of their potential applications in various electrochemical devices, high performance solid state batteries, energy conversion by fuel cells, super capacitors *etc*., because of their safety performance, ease of handling, shelf life, cyclability and processibility[1]. Solid polymer electrolyte for lithium batteries has many advantages over its counterpart liquid electrolyte, such as mechanical stability and processing flexibility, but its conductivity at room temperature is too low for practical application. Much attention has been focused on investigating the polymer electrolytes to enhance the ambient temperature conductivity by blending of polymer[2], plasticization[3], addition of nano fillers[4] *etc*. The plasticizers used are generally a low molecular weight aprotic solvent having a high dielectric constant, salt solvating power and sufficient mobility for ionic conduction are imparted by them. The low viscosity of the plasticizer decreases the T_g and increases the amorphous content, whereas higher dielectric constant of the plasticizer aids in ionic dissociation. The decrease in T_g results in an increase in the local chain flexibility which enhances the ion mobility[5]. But higher plasticization decreases the mechanical stability of the film which restricts its application as separators. In order to overcome this problem and retain the mechanical stability without compromising the conductivity nano particles are incorporated in the polymer matrix.

In the present work, PVC-PEG blend system is chosen as the matrix with propylene carbonate as plasticizer and $LiClO_4$ as dopant salt. Poly(vinyl chloride) manifests itself in a phase-separated morphology, because of its poor solubility in the liquid electrolyte, to provide a rigid frame work in the polymer electrolyte films[6]. However increase in PVC content decreases the ionic conductivity and poor adhesion which leads to increase in the interfacial resistance during repeated charge-discharge cycles. Propylene carbonate is selected as plasticizer for this system due to its higher dielectric constant. The low molecular weight polyethylene glycol (PEG) is chosen as it can act as a blend polymer as well as an additional plasticizer. The lithium perchlorate is chosen owing to its higher anionic radius and favorable for the polymer-salt complex formation. Zinc oxide is a wide band gap semiconductor with optoelectronic properties that make it an attractive candidate for a variety of device applications. Zinc oxide is versatile material that has found applications in solar cells, chemical sensors, electro luminescent devices, *etc*.[7,8]. The nano sized ZnO particles were synthesized through sol-gel method[9] and used as filler for this system.

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EXPERIMENTAL

Poly(vinyl chloride) (PVC) of average molecular weight 60,000 was purchased from Sigma-Aldrich. Poly ethylene glycol (PEG) (mol wt = 200) was procured from CDH, India. Propylene carbonate was purchased from Merck and $LiClO_4$ from sigma Aldrich. Tetrahydrafuran (THF) was procured from Merck and used as common solvent. The required quantity of PVC, PEG and $LiClO_4$ was dissolved in THF under constant stirring. After complete dissolution, ZnO particles are added and the resulting solution was stirred continuously for a period of 10-12 h. The resulting highly viscous slurry was cast on cleaned glass plate and the residual solvent was allowed to evaporate slowly at room temperature. Finally, mechanically stable, free-standing and flexible thin films were obtained and kept in desiccators for further drying.

The crystalline structure of the resultant electrolyte films was investigated using JEOL, JDX 8030 X-ray diffractometer. To study the conductivity behaviour of the polymer electrolytes, impedance spectroscopy was performed using a computer controlled micro Auto lab type III in the frequency rage 50 Hz-100 KHz. The samples were cut into proper sizes and sandwiched between indigenously designed two stainless steel electrodes. The conductivity (σ) was determined using the relation $\sigma = t/R_bA$, where, t is the thickness of the electrolyte, A, the electrode contact area and R_b is the bulk resistance obtained from the plots of real impedance Z_r against imaginary impedance Z_i (Table-1).

TABLE-1
COMPOSITION (wt %) AND IONIC CONDUCTIVITY VALUES OF POLYMER ELECTROLYTES AT ROOM TEMPERATURE

PVC	PEG	PC	$LiClO_4$	ZnO	σ at RT (S/cm)
25.0	15	50	10	0	0.687×10^{-6}
24.5	15	50	10	0.5	5.356×10^{-6}
24.0	15	50	10	1.0	2.725×10^{-6}
23.0	15	50	10	2.0	3.218×10^{-6}
21.0	15	50	10	4.0	6.052×10^{-6}
19.0	15	50	10	6.0	2.901×10^{-6}

RESULTS AND DISCUSSION

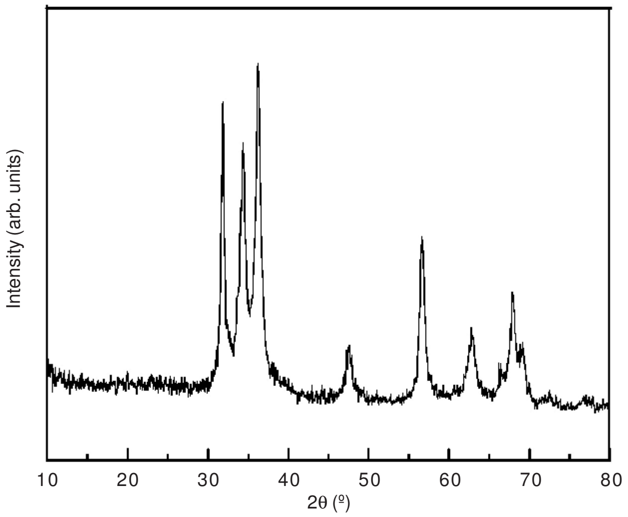

Fig. 1. X-Ray diffraction pattern of synthesized ZnO nanoparticles

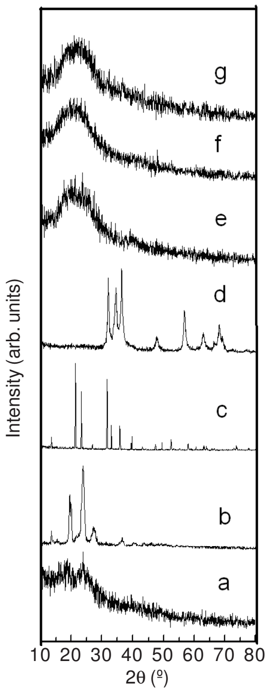

Fig. 2. X-Ray diffraction pattern a. PVC, b. PEG, c. $LiClO_4$, d. ZnO, e. film with 0 wt % filler, f. 0.5 wt % of filler, g. 4 wt % of filler

XRD analysis: Fig. 1 shows diffraction pattern of synthesized ZnO particles after calcinated at 400 ºC for period of 2 h. All diffraction peaks corresponding to the hexagonal ZnO (JCPDS card No. 36-1451) are observed. The pattern also coincides well with earlier reported results[10]. The average crystallite size of samples was determined by Debye Scherrer's formula: $D = k\lambda/\beta \cos \theta$, where k is a constant, the X-ray wavelength (0.154095 nm), β full wavelength at half maximum and θ is half diffraction angle. The average particle size determined using the above formula is 20 nm. Fig. 2 shows the diffraction spectra of pure PVC, PEG, $LiClO_4$, ZnO filler and the composite electrolyte film with 0, 0.5 and 4 wt % of filler. The broad peak corresponding to PVC reveals the amorphous nature of the polymer. The two prominent peaks of PEG (at $2\theta = 19.2°$ and at $2\theta = 23.4°$) show the crystalline nature of polymer. None of the peaks corresponding to $LiClO_4$ salt is found in the composite membrane indicating that the salt is well solvated by the constituents of the membrane. The diffraction patterns of composite films show a decrease in crystallinity than the pure polymer which is desirable property of the polymer electrolytes.

Conductivity analysis: Fig. 3 shows the variation ionic conductivity as a function of nano ZnO concentration. The maximum conductivity of of 6.052×10^{-6} S/cm at room temperature was observed for the system with composition (PVC:ZnO):PEG:PC:$LiClO_4$ = (21:4):15:50:10. The conductivity variation further features two maxima one occurring at 0.5 wt % of ZnO and at 4 wt % of ZnO filler. This type of conductivity variation in composite electrolyte systems are reported in earlier works[11]. The first conductivity maximum is associated with the creation of free ions as a result of addition of filler into the electrolytes. The decrease in the conductivity beyond the first maximum is related with the formation of ion

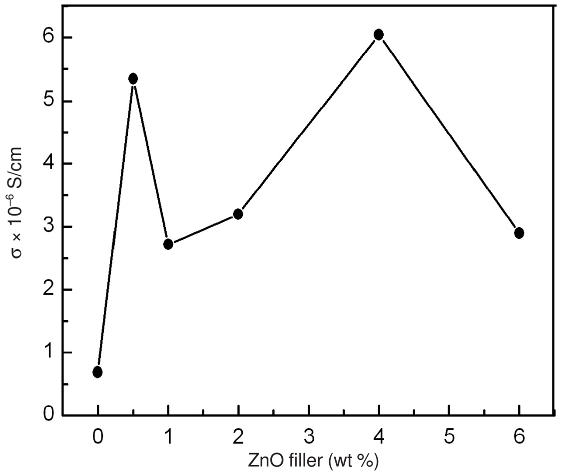

Fig. 3. Variation of conductivity with filler concentration (wt %)

pairs and bigger-sized ion clusters due reassociation of free ions when filler is added. The second maximum in the conductivity pattern is attributed to the composite effect and explained on the basis of the formation of a conducting interfacial space-charge double-layer between the nanosized ZnO particles and polymer gel electrolytes[12,13]. The decrease in conductivity after the second conductivity maximum is related to the blocking effect of filler particles, which hiders the motion of mobile ions[14]. An approximate 10 times enhancement in ionic conductivity is observed in the electrolyte with dispersion of 4 wt % ZnO filler with a substantial improvement in the mechanical strength.

Conclusion

The ZnO nanoparticles with average parrticle size 20 nm was synthesized through sol-gel method and incorporated as filler in PVC-PEG blend based plasticized polymer electrolytes with $LiClO_4$ as salt. The XRD anlysis reveals complete dissolution of salt and a slight decrease in the crystalinity of the membranes due to the addition of filler particles.The AC impedance studies indicates the stong influence of filler particles on the condutivity behaviour of the electrolytes.

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