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Structural and Electrochemical Properties of Polymer Blend Based ZnO Nanocomposite Solid Polymer Electrolytes by Spin–Coating Method

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The nanocomposite solid polymer electrolytes of Poly (ethylene oxide)/Polyvinylpyrrolidone doped with different concentrations (wt.%) of Zinc oxide nanoparticles (ZnO NPs) are prepared on quartz substrates using Spin-coat process. The Co-precipitation process is used to synthesize the ZnO NPs. The prepared nanocomposite polymer electrolytes were characterized by structural (XRD), morphological (SEM) and electrochemical (CV) studies. The spin-coating method is considered to be one of the most prominent due to the advantages of low cost and imperfection free uniform coating of resistant layers in the production of integrated circuits, surface coating and also acts as an intermediate insulator in different applications. The XRD analysis revealed the formation of nanostructures with (1 0 1) orientation in thin films which exhibits hexagonal Wartzite structure. All of the findings are correlated and discussed. The PEO/PVP/6 wt.% zinc oxide nanocomposite showed up to 500th cycles of reversible electrochemical response. The obtained results represent that nanocomposite solid polymer electrolytes based on ternaries are prominent materials for the use of transparent optoelectronic devices and solid-state batteries.

Keywords: Polymer blends electrolytes, ZnO NPs, XRD, Spin-coat, Solid-state batteries.

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1. INTRODUCTION

During 1970s Peter Wright and Michel Armand's discovery of polymer electrolyte (ionically conductive polymer) had introduced the first new class of solid ionic conductors; Michael Faraday had described in 1800s about the phenomenon of ionic conductivity in the solid state [1, 2]. The products of Faraday were solids like PbF_2F-ionic conductors. Polymer electrolytes are different from such materials in which they combine the solid state conduction of ions with its mechanical strength, which makes them absolute substitutes of electrolytes that are liquid in electrochemical cells, it is their good ability to make good interfaces with solid electrodes. Both solid state electrochemical products, such as lithium batteries, electrochrome displays and intelligent mirrors are highly sought after [3, 4]. Nonocomposite polymer electrolytes are prepared involving, first the dispersion of chosen ceramic powder (e.g., TiO_2, SiO_2 or Al_2O_3) and lithium salts (e.g., $LiClO_4$ or $LiCF_3SO_3$) in a low boiling solvent e.g., Acetonitrile, which is followed by adding the polyethylene oxide (PEO) which is the polymer component and by proper mixing of resulting slurry. The resulted slurry is later cast and the membranes are mechanically stable and homogeneous [5].

The method of spin coating is presently the prime technique used in producing thin uniformed films of photosensitive organic materials the range of micrometer and nanometer thicknesses. More than fifty years ago the pioneering analysis of spin coating was performed [6], which considered the thin spreding of axisymmetric film of the Newtonian fluid used on planner substrates which rotates with a constant angular velocity. The coating fabric is a polymer at many instances which is in the form of the solution that evaporates. Basically the spin coating is studied in making paint and pitch coating the polymer blends have received a tremendous amount of attention because of the improved properties of new material when compared to the earlier polymers in a simple way [7-9]. The polymer blending technique offers a wide range of improvements, including mechanical properties, resistance to fractures, chemical resistance, barriers and thermal properties.

Nowadays the rapid growth of the nanoscales gives us a new opportunity to utilize blends of polymer as matrix for incorporating the nanosized particles, nano becomes more versatile as an interconnecting network between the blend. Because of their wide potential use in development of new nanodevices, nanostructure materials have recently attracted much attention from researchers. The utilization of organic and inorganic polymer composite materials has lead to interest in the development of new materials and devices. The unique properties such as direct band gap (3.37 eV), n-type semiconductors with large excitation binding energy (60 eV) at room temperature, II-VI group zinc oxide (ZnO) is attracted and has numerous attractive features for electronics and optoelectronic devices [10-12].

Many experimental and theoretical results suggest that ZnO has many properties that will make it the ideal composite material to building a new generation of nano-electro, sensors, and transistors mechanism devises, display devices optoelectronic devices and solar cells. The interest in mixing organic and inorganic materials for a wide range of applications by altering their electrical and optical properties is growing [13, 14]. Researchers have recently have given a report that PVA/ZnO can be utilized in different fields and in production of composites that are mechanically strong

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enough. The PEO and PVP-based polymer blend electrolytes with cobalt chloride ($CoCl_2$), lithium perchlorate ($LiClO_4$) and polyimide-PEO doped with $LiCF_3SO_3$ are reported [15-17]. The nanoparticles could have effect on the bulk properties of the blend, since the particle performs a key function in converting its properties. The literature record suggests that polymer nanocomposites where studied notably and several properties of polymer composites are reported [18]. But, there are no reports on Zn^{2+} nanoparticle ion doped polymer blend and its influence on structural and electrochemical properties. In this case, PEO/PEP blend was used because of their functional groups like oxygen linked with ether in polyethylene oxide and double bond oxygen group linked with main chain in polyvinylpyrrolidone [19].

The doping of the ternary based polymer nanocomposite electrolytes of Poly (ethylene oxide), Polyvinylpyrolidone is done by different concentration (wt.%) of the nanoparticles of Zinc oxide (ZnO NPs; which are synthesized by Co-precipitation method), and are prepared using Spin-coat method on quartz substrates. The prepared samples were characterized structural (XRD, SEM) and electrochemical properties. All the results are correlated and discussed.

2. EXPERIMENTAL SECTIONS

2.1 Materials used and Synthesis of ZnO Nanoparticles

By the Co-precipitation method the nanoparticles of the zinc oxide are the synthesized [20], using zinc nitrate hexahydrate ($Zn(NO_3)_2\ 6H_2O$), Sodium hydroxide (NaOH) were analytical grade chemicals are bought from Sigma-Aldrich which is an American chemicals company and by the using double distilled water they are utilized directly without extra purification.

Sodium hydroxide (NaOH) of 50 ml of 1 M is added drop-wise to conical flask which contains 100 ml of 0.1 M concentration of Zn $(NO_3)_2\ 6H_2O$. The solution which is obtained is centrifuged and the powder obtained is washed in double distilled water for 5-6 times the powder obtained is dried in an oven with hot air at 110 °C for about 6 hours to obtain nanopowder of ZnO.

2.2 Preparation of PEO/PVP/ZnO Film Using Spin-coat Method

Using the spin-coat method the composites of PEO/PVP and the synthesized ZnO NPs (PEO/PVP/ZnO) are coded as PNCs electrolyte (Polymer nanocomposites, PNCs) which are prepared in weight ratios of (50/50/0, (48/48/4) and (47/47/6) with constant stirring for about 10–12 hours. The PEO and PVP (Figure 2.1(a) Molecular structure of PEO, PVP, ZnO NPs and its polymer nanocomposite thin film) are dissolved in methanol separately, both solutions are mixed and the desired amount of synthesized ZnO NPs (4 and 6 wt.%) is added to the solution polymer blend. The solution will be stirred until a homogeneous viscous and the possible interaction is expressed in figure 2.1(b), then each solution polymer is dropped onto the surface of the quartz plate placed on a spin-coater with the help of micropipette and does the polymer thin film is prepared. The conditions of the spin-coating are as follows the speed of the 3000 RPM is for about 40 sec and for 6000 RPM it is 50 sec. The spin-coating of the PNCs solution is done by three repetitions, the transparent and uniform thickness film is finally obtained (Figure 2.1c) where found in the range 3.9 ~ 4.2 μm (Figure 2.1d (Cross-sectional SEM image)).

2.3 Characterizations

The electrolyte of PNCs are characterizations and identified by a structural phase by the X-ray diffraction (XRD) using X-ray diffractomater (Rigaku Miniflex) with

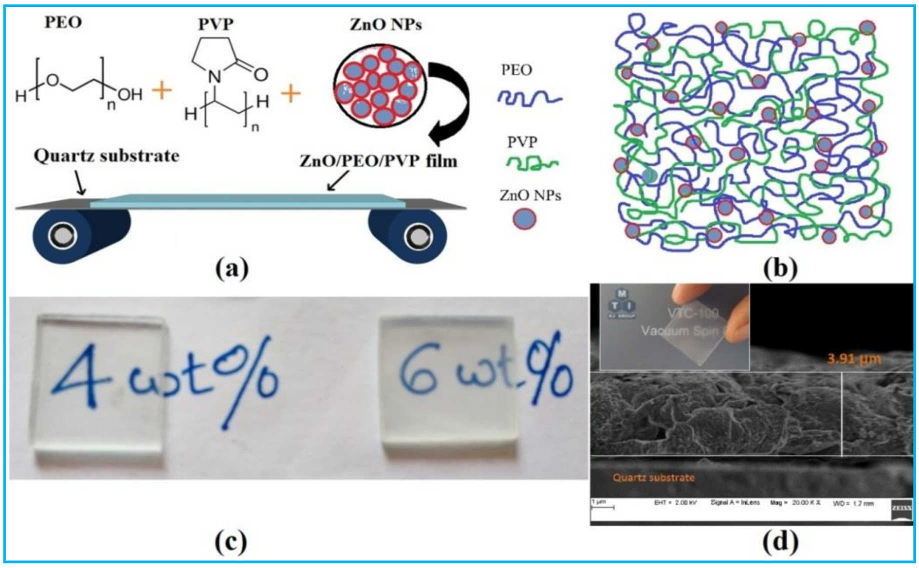

Fig. 2.1 – (a) The PEO, PVP, ZnO NPs Molecular structure and its polymer nanocomposite thin film on quartz substrate, (b) possible interaction of polymer chains PVP (Green chains), PEO (Blue chains), and ZnO NPs (red circled grey points), (c), High optically transparent PNCs thin film, (d) Cross-sectional SEM image of thickness 3.91 μm (Inset: Optical photograph of transparent PNCs electrolyte) [20]

Table 3.1 – Structural parameters for the electrolytes of ZnO NPs and PNCs: Bragg angle (2θ), peak height / maximum intensity (I), interplanar distance (d), average crystallite size (τ), dislocation density (δ) and lattice strain (ε)

Sl. No.	Sample Code (wt.%)	2θ (deg.)	I (a.u.)	d (Å)	τ (nm)	δ ($\times 10^{14}$) (lines/m^2)	ε ($\times 10^{-2}$)
1	ZnO NPs	36.24	4063	2.476	18.29	29.89	1.26
2	PEO/PVP(50/50)	19.31	11306	4.592	17.58	32.36	2.44
3	PEO/PVP/ZnO NPs (48/48/4)	18.96	12606	4.676	29.33	11.62	1.49
4	PEO/PVP/ZnO NPs (47/47/6)	18.97	3421	4.674	11.17	80.15	2.91

CuKα radiations ($k = 1.5418$ Å). The morphology of the surface is studied using a SEM (Scanning electron microscope) the model used is Sigma Zeiss Carlzeish. The CHI660E electrochemical workstation (CH-Instruments, USA) is used to perform an electrochemical measurement and the sample should be sandwiched in between stainless still electrodes (SS/Electrolyte film/SS).

3. RESULTS AND DISCUSSION

3.1 X-Ray diffraction analysis

The Figure 3.1 gives us an X-ray diffraction pattern of pure ZnO NPs, blend of pure PEO/PVP and PNCs electrolytes in the range $2\theta = 10$-60° to examine the crystalline structures. The most sharp and intense peaks are observed here which indicate the synthesized ZnO NPs which are highly crystalline nature with a single phase. The diffraction of the peaks appearing at the 2θ angles 32.18, 35.09, 37.01, 48.12 and 57.01 which are found to be corresponding to the planes (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0), respectively.

The observed peaks which are indexed are found to be good agreement with JCPDS file number 80-0074 and it is indexed as the hexagonal Wurtzite structure of ZnO with a space group of p63mc and is consistent with the crystal structure similar value has also been reported [21]. The X-ray diffraction patterns of pure blend PEO/PVP exhibited the presence of two sharp peaks, one is at $2\theta = 19.21°$ (1 2 0) and another at $2\theta = 23.25°$ (1 1 2) for 50 wt% each polymer matrix. The new lowest diffraction peaks appears at 31.62°, 34.25°, 36.18°, 47.36° and 56.58° it shows the presence of Zn^{2+} in the polymer blend matrix of PEO/PVP. The average crystalline size (τ), inter planar distance (d) calculated values are tabulated in Table 3.1. The dislocation density (δ) is a measure of the amount of crystal defects and vacancies, its shows in the Table 3.1 that δ increases from 32.36×10^{14} to 80.15×10^{14} with increasing ZnO wt%. It shows that imperfection in the lattice increases with particle size. In general, difference in micro-strain can be due to the change in particle microstructure, size and shape, and defects. Such findings support the decrease in the size of the crystallite and even in the amorphous regions. Their estimated values are depicted in Table 3.1. The improvement of the amorphous region results in the fast mobility of the ions from one site to another site; hence the ionic conductivity is significantly improved [20, 22].

As the ZnO NPs concentration increases in the polymer bled mixture, the intensity of the peaks is seen to gradually decrease and become relatively broad, indicating a decrease in the degree of crystallinity. These observations are well confirmed with Hodge et al., that is, the correlation between the peak intensity and the degree of crystallinity [23].

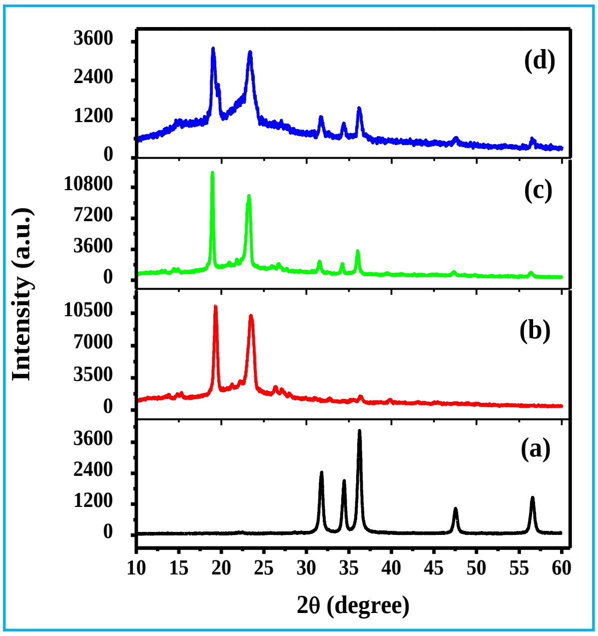

Fig. 3.1 – X-ray diffraction of (a) ZnO NPs, (b) PEO/PVP blend and pure blend doped with (c) 4 wt.% and (d) 6 wt.% ZnO NPs

3.2 Morphology Studies

To investigate the effect of ZnO NPs and to study the dispersion of NPs in a polymeric blend matrix scanning electron microscopy is used. Figure 3.2 shows the nanostructures of ZnO and PNCs with different wt.% of Zn^{2+} NPs. The particles are found to be roughly spherical and homogenous, few of them are rod-like structures, but most of them are spherical, dramatically arranged into the spindle shaped morphology; the individual ZnO NPs have the length about 90-210 nm range as shown in Figure 3.2(a). The surface of the films becomes rough with small particle (white spots) aggregates, when the content of ZnO is 4 wt.% which is shown in Figure 3.2(b), it indicates homogeneous segregation of ZnO NPs in the polymer blend system.

Further increase in the concentration of ZnO (6 wt.%) also shows the presence of ZnO NPs on the surface and the formation of the cracks on the surface of the blended matrix are observed as shown in Figure 3.2(c). This result further shows an adhesion between the surface of ZnO NPs and the polymer blend matrix [24].

Polarized Optical Microscopy (POMs):

Figure 3.3 reveals that 4 wt percent of PNCs photographs shows blackish region known as amorphous region, but the 6 wt percent photograph of ZnO NPs polymer electrolyte film indicates a rise in black dots. It

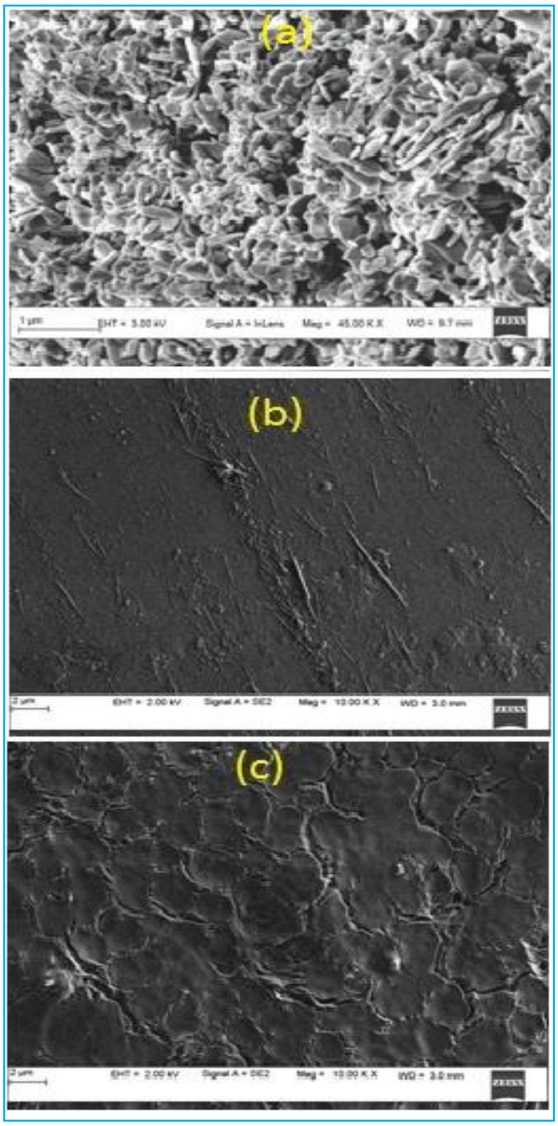

Fig. 3.2 – SEM micrographs: (a) synthesized ZnO NPs, (b) 4 wt.% and (c) 6 wt.% of ZnO NPs doped polymer blend matrix

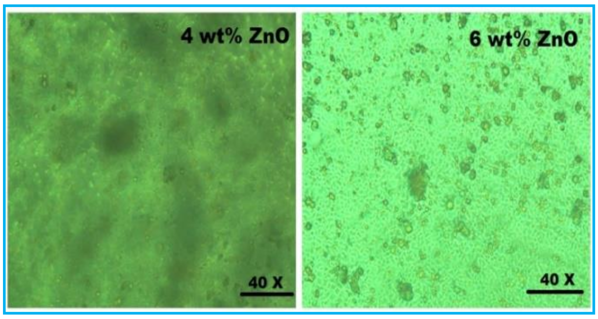

Fig. 3.3 – Optical micrograph images of the PNCs deposited on substrates of quartz with various wt. percentages ratios

indicates an increase in the film's amorphicity, and thus increases the conductivity.

3.3 Electrochemical Studies

The electrochemical stability window of the PNCs electrolyte is determined by line as sweep voltametry (LSV) and the performed the measurements were in the potential range of 0 to 5 V at different scan rates from 10-100 mV/s as shown in the Figure 3.4(a). When the current is applied the potential difference increases linearly and clearly indicating the semi conductors behavior. The conducting behaviour of PNCs with the 6 wt.%, the constantly increases respect to the current applied as well increasing scan rates. The Figure 3.4(b) shows the cyclic voltammaograms (CVs) recorded for 6 wt.% PNCs electrolyte with a scan rate of 50 mV/s in the voltage range between – 2.2 and 1.5 V.

To study the chemical and electrochemical stability of PNCs the CVs are cycled up to 500 times. After the initial scan, one can see that the electrochemical response remains to be same for entire 500th cycles (scans) assuming the robust nature of the material. The rectangular and symmetric current-potential (I-V) characteristics of a capacitor are clearly shown by them for a typical capacitative behaviour of the appearance of rectangular shaped CV as been well documented [25].

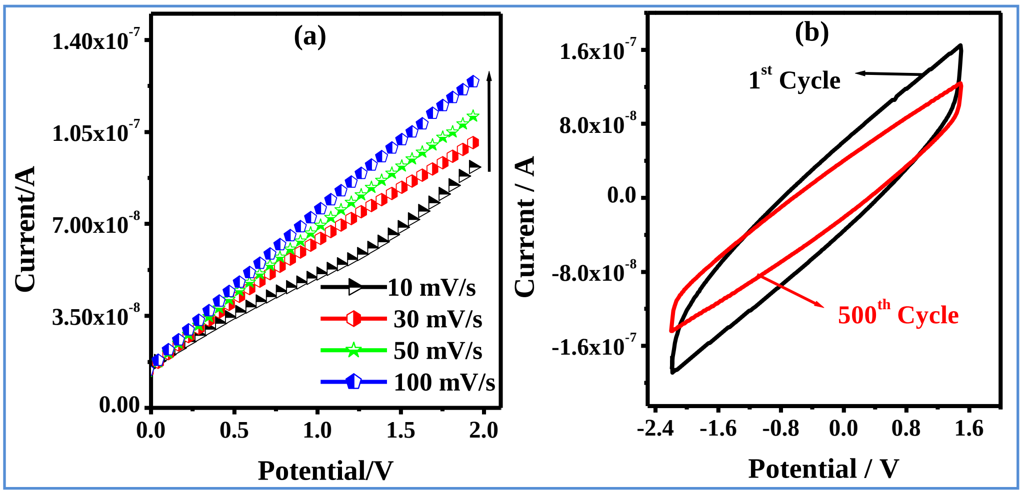

Fig. 3.4 – (a) Linear Sweep Voltammogram (LSV) at different scan rates, (b) Cyclic Voltammograms (CVs) at scan rate 50 mV/s for 6 wt% PNC electrolytes

4. CONCLUSIONS

The syntheses of zinc oxide nanoparticles (ZnO NPs) by Co-precipitation technique are successfully obtained. The ternary based solid polymer nanocomposites (PNCs) thin films of Poly (ethylene oxide)/Polyvinylpyrrolidone doped with various wt.% (4 and 6 wt.%) of Zinc oxide nanoparticles are prepared by spin-coat method on quartz substrates. The formation of nanostructures in thin films exhibiting hexagonal wurtzite structure with (1 0 1) orientation was revealed by XRD analysis. The cyclic voltametry revealed the PEO/PVP-6wt% ZnO composite showing a reversible electrochemical response up to 500th repeated cycles. The obtained properties of such as optical, electrical and dielectric of the PEO/PVP-6 wt.% ZnO NPs composite are suitable for the application of integrated electronic device and the solid-state batteries.

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