



Synthesis and characterisation of gel polymer nanocomposite (PVP-PEG-nano ZnO) electrolyte for solar cell applications

Hari Hara Priya G¹, Sivakumar E. K. T², Suganya N¹ and Jaisankar V^{1,*}

¹PG and Research Department of Chemistry, Presidency College (Autonomous), Chennai-600005, India.

²Centre for Nanoscience and Technology, Anna University, Chennai 600 025, India.

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ABSTRACT

Ionically conducting polymer electrolytes are important materials for practical applications in solar cells, high energy density solid-state batteries, super capacitors, fuel cells, sensors and electrochemical devices. Dye-sensitized solar cells (DSSCs) have been attracting intensive interest for scientific research and industrial applications owing to their low fabrication cost, environmentally friendly operation and relatively high efficiency. In order to improve the efficiency of DSSCs, many efforts on modification of polymer gel electrolyte have been made through synthesizing new polymers or adding inorganic nanofillers. Hence, we report on the synthesis of polymer nanocomposite electrolyte consisting of polyvinylpyrrolidone-polyethylene glycol (PVP-PEG)/nano ZnO/KI/I₂. Zinc oxide nanoparticle synthesized by sol-gel method is used as inorganic nanofiller. Polymeric nanocomposite electrolyte was prepared by blending polymer with ZnO nanoparticle using solution-casting technique. The property of nanocomposites depends mainly on the chemistry of polymer matrices. The dispersion of nanoparticles in the polymer matrices is a general prerequisite for achieving desired mechanical and physical properties. ZnO nanoparticles and polymer nanocomposite were characterised by Ultraviolet-Visible (UV-Vis) spectroscopy, Fourier Transform Infra Red (FT-IR) spectroscopy, X-Ray Diffraction (XRD) analysis and Field Emission-Scanning Electron Microscopy (FE-SEM). The effect of structural modification of material on conductivity of polymer and its composite was evaluated and compared by SEM and electrochemical impedance spectroscopy. The polymer nanocomposite electrolyte synthesised have its practical application in the fabrication of DSSC.

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Introduction

The worldwide demand for energy has been massively increased. In order to sustain global political, economic and environmental stability, it is necessary to get an abundant supply of energy. Moreover, the development of carbon-free sources of energy becomes one of the major scientific challenges for us. As a potential alternative energy resource, solar energy has received extensive attention around the world. The dominance of the photovoltaic market by inorganic solid-state junction devices is now being challenged by the emergence of a third generation of cells. Among them the dye-sensitized solar cell (DSSC, also known as Grätzel cell) with a new type of charge separation mechanism is a promising potential candidate capable of meeting our future energy demands [1]. A conventional DSSC is constructed by an electrode consisting of a porous TiO₂ layer with dye adsorbed on the TiO₂ surface, organic liquid electrolyte solution containing a I⁻/I₃⁻ redox couple, and a platinum-coated counter electrode. The electrolyte is an important component in determining the efficiency and durability of DSSCs. Overall light-to-electric conversion efficiency up to 12% of DSSCs has been achieved with liquid electrolytes [2], however, the liquid electrolytes create significant technological problems such as leakage, evaporation of solvent, high-temperature instability and flammability, dye degradation and electrode corrosion, which have restricted the practical application of DSSCs [3]. By addressing these issues, quasi-solid-state/full-solid-state electrolytes, such as ionic liquid-based gel electrolytes [4],

polymer gel electrolytes [5] and solid polymer electrolytes [6] have been made to replace liquid electrolytes. Among these species, the quasi-solid-state polymer gel electrolytes have been attracting a great deal of interest because of their nonflammability, negligible vapor pressure, good contact with the nanocrystalline TiO₂ anode and Pt counter electrode [7,8]. However, DSSCs employing polymer gel electrolytes have exhibited low cell efficiency. In order to improve the efficiencies of quasi-solid-state DSSCs, many efforts on modification of gel electrolyte have been made through synthesizing new polymers [9], or adding inorganic nanofillers [10-12]. Researchers have reported that the addition of nanoscale ceramic fillers (i.e., SiO₂, Al₂O₃, ZnO and TiO₂) [13-15] and clays [16] into polymer electrolytes not only improved the ionic conductivity but also enhanced the mechanical strength and stability of the polymer electrolyte. The enhancement in the conductivity is predominantly due to the increase of amorphous region in the polymer as a consequence of the dispersal of the filler particles.

Wei et al [17] reported that ZnO nanoparticles will enhance the efficiency of DSSCs. For example, ZnO in many different nanostructural forms were used as photoanode. ZnO has shown a great deal of research interest in DSSCs due to some of its fascinating properties. Nanostructured ZnO has unique properties like transparent n-type semiconductor with direct wide band gap (3.37 eV), nontoxicity, high chemical stability and high electron transfer capability.

The preparation methods of polymer electrolytes include the copolymerization [18], the cross-linking [19], the plasticization [20] and so on. Polymer blending also is a useful technique for designing polymer electrolytes with a wide variety of properties [21]. An important commercial advantage is that polymer blends offer a way to produce new materials by using polymers existed, which thus reduces preparation costs [22].

Various semisolid gel electrolytes have been designed and used in DSSCs and reported in the literature [23–26]. Among them, the electrolyte containing of KI and I₂ dissolved in a blending polymer of polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG) is a good candidate for the preparation of the new solar cells [27]. It is observed that the addition of ZnO nanoparticles can be effective to reduce considerably the recombination process and then the efficiency of the cell. Our attention was drawn to PVP/PEG blending polymer electrolytes based on the following reasons: (a) Polyvinyl pyrrolidone (PVP) deserve a special attention among the conjugated polymers because of good environmental stability, easy processability and moderate electrical conductivity [20]. (b) Polyethylene glycol (PEG) is a photochemical stable polyhydric linear polymer, it was used as a polymer host and prevents the PVP volatilizing and leaking to form a stable polyblend electrolyte [28].

In this paper, we report on the effect of addition of n-ZnO to a gel polymer electrolyte to study the conductivity of gel polymer electrolyte which is used to increase the energy conversion efficiency of DSSCs. Gel polymer electrolytes were prepared by adding KI and I₂ to PVP/PEG blending polymer. The results obtained in this study could play an important role in determining the future direction for the development of high performance gel polymer electrolytes.

Experimental

Materials

All chemicals used were of analytical grade and have been used without purification. Zinc nitrate (Zn(NO₃)₂) and sodium hydroxide (NaOH) were purchased from SD fine chem., India. Anhydrous ethanol, iodine (I₂) and potassium iodide (KI), were purchased from Merck.

PVP (Mw 40000) and PEG (Mw 6000) were obtained from Loba Chemie.

Synthesis of nano-zinc oxide

To the 100 ml of hot 1M NaOH solution 100 ml of 0.5 M Zn(NO₃)₂ was slowly added in drops with stirring. The precipitated ZnO was stirred for 2 hours. Then the precipitate was washed several times with deionized water, dried at 80°C in an oven for 5 hours and calcined at 600°C for 2 hours to obtain nano-ZnO powder.

Synthesis of gel polymer electrolyte (PE)

Polyblend electrolytes of PVP blend PEG (PVP:PEG-40:60) with KI (0.20 mmol g⁻¹ polymer) and I₂ (0.1 mmol g⁻¹ polymer) (PE) have been prepared by means of solution mixing method using anhydrous ethanol as solvent. The mixture were stirred vigorously at 60–65°C in a sealed glass vessel for 5 to 6 hours to form a homogeneous mixture and then the glass vessel is unsealed to evaporate the solvent and a viscous gel was obtained [27].

Synthesis of gel polymer nanocomposite electrolyte (PNE)

10 wt% of n-ZnO was added to the prepared gel polymer electrolyte. The mixture (PNE) were stirred vigorously at 60–65°C in a sealed glass vessel for 5 to 6 hours to form a homogeneous mixture and then the glass vessel is unsealed to evaporate the solvent and a viscous gel was obtained [29].

Characterisation

The prepared n-ZnO, gel polymer electrolyte and gel polymer nanocomposite electrolyte were characterized by UV-Vis spectra, IR spectra, XRD, SEM and TG analysis. The UV-Vis absorption spectra of the samples were recorded in the range of 200–400 nm by UV-Vis spectrophotometer. IR spectra were recorded using a PerkinElmer IR spectrometer in the range of 4000 cm⁻¹ to 400 cm⁻¹. The samples were embedded in KBr pellets. For XRD analysis a Siemens D500 diffractometer with CuKα filtered radiations was used for assessing the structure and crystallinity. The samples were scanned over the 2θ range from 10° to 90°. The crystallite size (D) of the nanoparticles was calculated from XRD using the Scherrer equation:

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

The structure and morphology were studied using a HITACHI S-3000 scanning electron microscope (SEM). Thermal stability of new gel polymer nanocomposite electrolyte was measured by a STA 409PC/PG TGA device under argon atmosphere over a temperature range of 30°–500°C at a heating rate of 10°C min⁻¹. The conductivity of gel polymer and polymer nanocomposite electrolyte was measured by electrochemical impedance spectroscopy and compared.

Results and Discussion

UV-Vis Spectra

Absorption spectroscopy is a powerful non-destructive technique for exploring the optical properties of semiconducting nanoparticles. The absorption spectra of n-ZnO in the UV range are presented in Fig. 1.

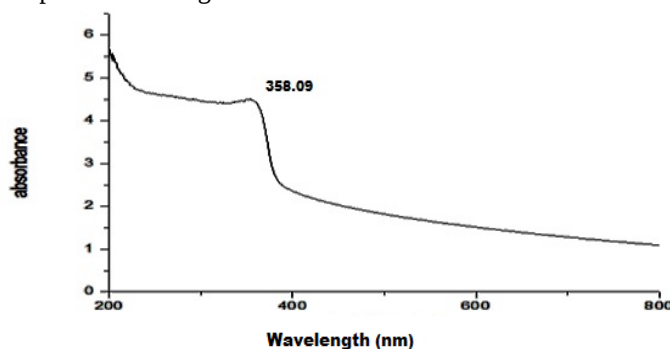


Figure 1. UV-Vis spectra of n-ZnO

The strong absorption band of λ_{max} at 358 nm showed the presence of ZnO nanoparticles which is shifted to blue region with respect to the bulk absorption edge appearing at 380 nm [30]. The absorption edge systematically shifts to the lower wavelength or higher energy with decreasing size of the nanoparticle.

Fourier-Transform Infrared (FTIR) spectroscopy

FT-IR spectra recorded for n-ZnO, PE and PNE are presented in Fig. 2.

Figure 2(a) shows the FTIR spectrum of the ZnO nanoparticles synthesized by sol-gel method. The characteristic absorption peak at 476 cm⁻¹ due to Zn-O vibration authenticates the presence of ZnO. The IR spectra of PE and PNE are also shown in Fig. 2(b) and (c). The peak at 1663 cm⁻¹ is due to carbonyl stretching, 1283 cm⁻¹ corresponds to the N-C vibration, 2887 cm⁻¹ is attributed to CH₂ stretching, 1112 cm⁻¹ is assigned to C-O-C stretching, 3459 cm⁻¹ corresponds to O-H stretching and 525 cm⁻¹ corresponds to presence of metal oxide in nanocomposite. The shift in the vibrational frequency for n-ZnO in Fig. 2(c) confirms the formation of polymer nanocomposite electrolyte.

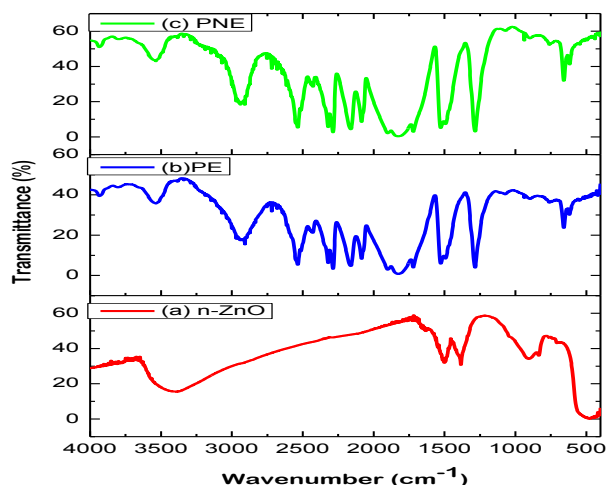


Figure 2. FTIR spectrum of pure ZnO nanoparticles, PE and PNE

X-Ray diffraction analysis

The X-ray diffraction analysis is a powerful tool to determine the structure and crystallization of the polymer matrices. In order to investigate the effect of blending, XRD analysis was performed. The diffraction patterns of the n-ZnO, PE and PNE are shown in Fig. 3.

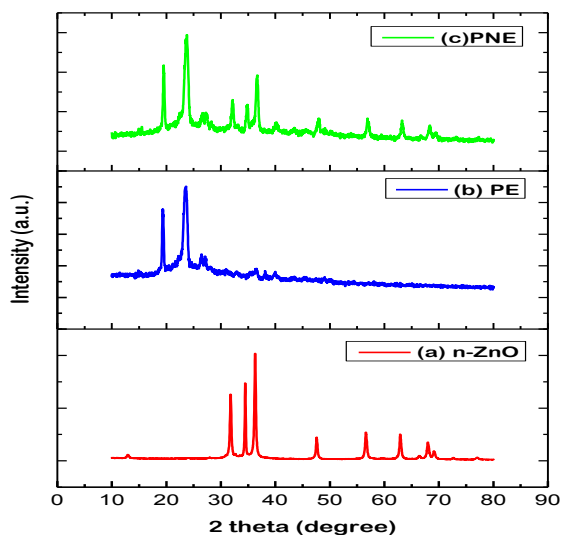
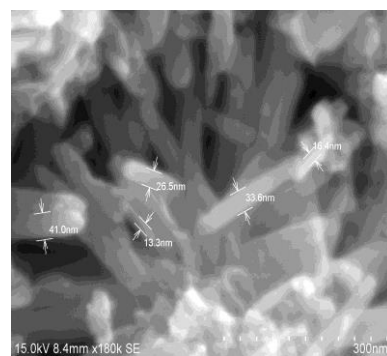


Figure 3. X-ray diffraction patterns of the n-ZnO, PE and PNE

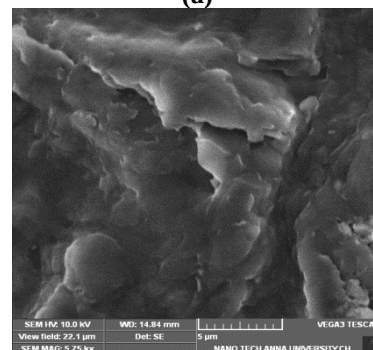
The average particle size of n-ZnO was calculated from the XRD (Fig. 3a) using Scherrer formula and was found to be around 35 nm. The XRD patterns of PE and PNE are also compared in Fig. 3(b) and (c). It is observed that although the peak positions of PE and PNE remains unaltered, the relative intensity of peaks in PNE decreases sharply at $2\theta=24^\circ$ indicating the amorphous nature of the PNE and also appearance of new peaks, which implies that all ingredients (PVP, PEG, KI, I_2 and n-ZnO) were mixed properly to form a gel. It is well known that amorphous state of the polymeric gel is desirable for the carrier transport and the ionic conductivity [31].

Scanning Electron Microscopy (SEM)

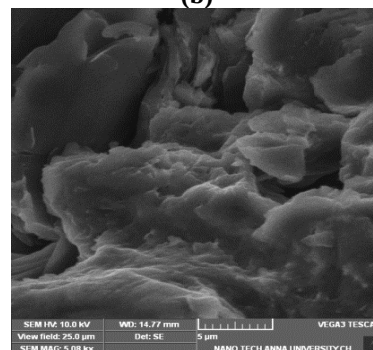
SEM images (Fig. 4) were used to evaluate the surface morphology of ZnO nanoparticles, PE and PNE.



(a)



(b)



(c)

Figure 4. SEM images of (a) n-ZnO, (b) PE and (c) PNE

Figure 4(a) shows the SEM morphology of the synthesized n-ZnO particles. It demonstrates clearly that the formation of ZnO nanorods with the average size range of 15-45 nm which is in close agreement with the size calculated by Scherrer formula based on the XRD pattern. Figure 4(b) and (c) shows the SEM morphology of the synthesized PE and PNE respectively. From Fig. 4(c) it can be seen that the introduction of the n-ZnO into the polymer matrix produces dramatic morphological changes to the host polymer structure and the crystallinity of the polymer decreases considerably. The existence of two distinct phases was confirmed, the first phase corresponds mainly to the original polymer matrix and is crystalline, the second phase is an amorphous area consisting of polymer subunits held together forming straight long chains along which ZnO nanoparticles are distributed. Therefore, the polymer chains separated by the ZnO are arranged in a three-dimensional stable network that creates free space and voids into which the iodide/triiodide anions can easily migrate.

Thermogravimetric analysis of PNE

In order to investigate the thermal stability of the gel polymer nanocomposite electrolyte (PNE), thermogravimetric analysis was carried out on the sample dried under vacuum at 60°C (Fig. 5).

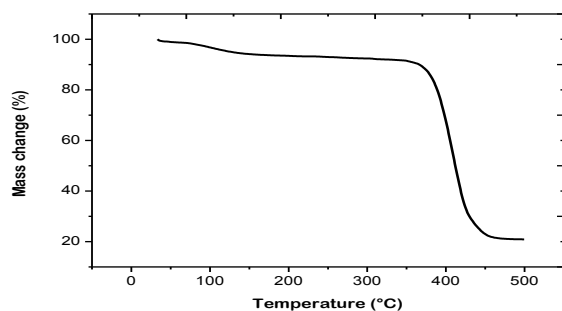


Figure 5. TGA thermogram of PNE

From the TGA thermogram, it can be observed that before thermal degradation, the gel undergoes weight loss gradually, at temperature less than 100°C which is due to the existence of ethanol and water residue in electrolyte. Thermal degradation of the gel electrolyte occurs at temperature greater than 350°C with a weight loss of 71%. Complete thermal degradation extends above 500°C is due to the presence of n-ZnO in the polymer nanocomposite electrolyte. This high thermal stability of the gel is beneficial for fabricating a desirable DSSC.

Conductivity study of PE and PNE

The electrochemical impedance spectroscopy is an excellent tool to characterise the electrochemical properties of the materials and their interfaces with the electronically conductive electrodes. The ionic conductivity of PE and PNE was calculated using Nyquist plots (Fig. 6) obtained from electrochemical impedance spectroscopy. The bulk resistance (R_b) value is given by the intercept obtained on the real axis in the plot of real versus imaginary component of impedance. The conductivity (σ) of the polymer electrolyte was calculated using the relation,

$$\sigma = t/A \times R_b$$

where t is the thickness of the polymer electrolyte and A is the contact area of the sample.

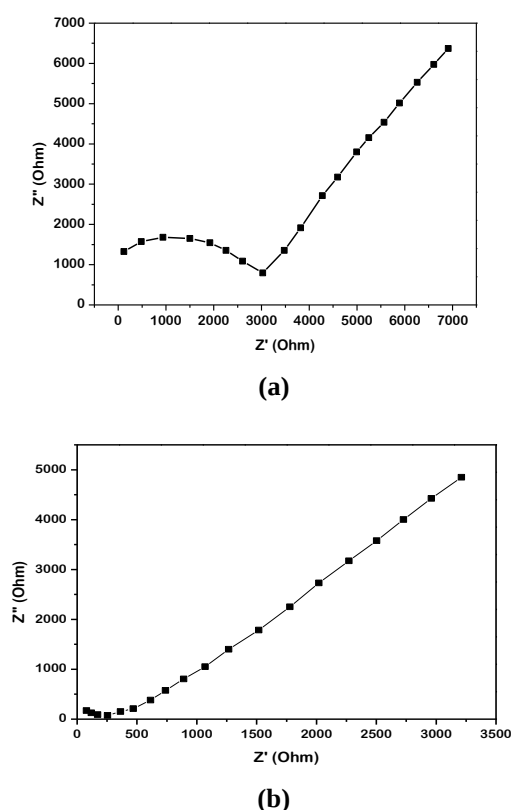


Figure 6. Nyquist plots of (a) PE and (b) PNE

The ionic conductivities of polymer electrolyte and polymer nanocomposite electrolyte are found to be $2.92 \times 10^{-7} \text{ S cm}^{-1}$ and $4.22 \times 10^{-6} \text{ S cm}^{-1}$ respectively. The increase in conductivity of polymer nanocomposite electrolyte was due to the presence of n-ZnO.

Conclusion

A new quasi-solid-state electrolyte containing PVP, PEG and n-ZnO was prepared for the purpose of improving the cell performance for practical application in dye-sensitized solar cells. UV-Visible spectra confirm the formation of n-ZnO particles. FTIR confirms the presence of n-ZnO in the prepared polymer nanocomposite electrolyte. XRD analysis reveals the amorphous nature of the PNE due to n-ZnO. The morphology of the electrolytes using SEM analysis explains the changes in the phase of polymer. The structural modification in PNE results in the enhancement of the mobility and hence the ionic conductivity. TGA analysis proves the thermal stability of the PNE. Conductivity study shows increase in conductivity for PNE due to incorporation of n-ZnO. This polymer nanocomposite electrolyte can be used in DSSCs to increase the energy conversion efficiency.

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