

Research Article

Effect of Nano TiO₂ on Ionic Conductivity of Polymer Nanocomposite Gel Electrolyte

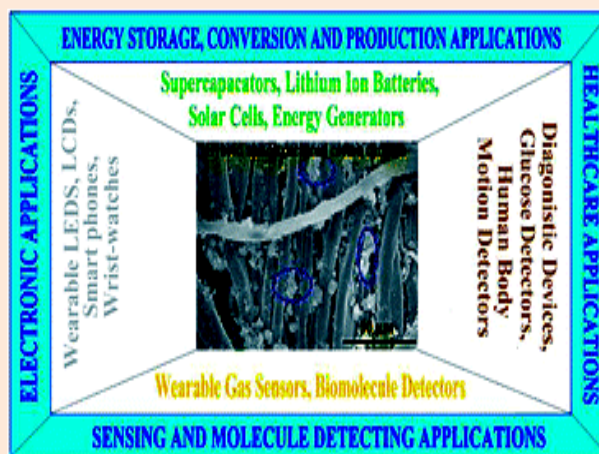
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Abstract

Polymer blends offer a practical and efficient way to fulfill novel requirements for material properties and applications. In the present work we have prepared a polymer blend electrolyte comprising of polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and nano titanium oxide (n-TiO₂) as filler. The polymer blend electrolyte was developed as a film by solution casting technique, with varying ratio of the filler. X-ray diffraction (XRD) revealed that the incorporation of n-TiO₂ into the blend suppresses the crystallinity of PVP. The prepared polymer nanocomposite electrolyte was characterized by Fourier transform Infrared spectroscopy (FTIR), Ultraviolet – visible spectroscopy (UV). The structural morphology was characterized by Scanning electron microscopy (SEM). The ionic conductivity was studied using Electrochemical Impedance Spectroscopy (EIS).

Keywords: polymer blend, solution casting technique, Ionic Conductivity, electrochemical Impedance Spectroscopy

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Introduction

Polymer electrolytes are used as promising materials in electrochemical devices such as rechargeable batteries, fuel cells, supercapacitors, electrochromic displays, etc. The area of polymer electrolytes has gone through various developmental stages, i.e. from dry solid polymer electrolyte (SPE) systems to plasticized gels, rubbery to micro/nano-composite polymer electrolytes. The gel polymer electrolytes have currently exhibits worldwide attention due to their excellent mechanical and chemical stability. Generally, gel polymer electrolytes are composed of a host polymer material by injecting liquid electrolytes into the small pores of the polymer matrixes. By dispersion of nanofiller in gel polymer electrolytes, improves the dimensions as well as electrical and electrochemical properties of the gel system. Such composite gel electrolytes preserve a porous structure due to dispersion of filler, which improves the adsorption of liquid electrolytes and reduced reactivity, reduced leakage, improved safety, better shape flexibility and manufacturing integrity. The advantages of incorporating the fillers are twofold. One is the enhancement in ionic conductivity at low temperatures and the other one is to improve the stability at the interface with electrodes [1–8].

Polyvinylpyrrolidone (PVP) has drawn a special attention amongst the conjugated polymers because of its good environmental stability. PVP is a potential material having a good charge storage capacity, high dielectric strength, low scattering loss and dopant dependent electrical and optical properties. Chemically PVP has been bound to be inert, nontoxic and it displays a strong tendency for complex formation with a wide variety of smaller molecules. PVP is an amorphous polymer and due to the presence of the rigid pyrrolidone group, which is known to form various complexes with many inorganic salts. Polyethylene glycol (PEG) is a photochemical, stable polyhydric linear polymer. It was used as both reactant and plasticizer [9]. The conductivity properties of polymer depends upon the reactivity of dopant. Since K⁺ is a fast conducting ion in a number of crystalline and amorphous materials, its incorporation in polymeric system enhances the electrical performance.

Hence, in this work we studied the ionic conductivity of polymer nanocomposite electrolyte system composed of polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG) as polymer blends, Potassium Iodide(KI)-Iodine(I₂) as redox couple, and nano TiO₂ as filler.

Experimental

Materials

Titanium (IV) isopropoxide (TTIP, 97%, Sigma Aldrich), isopropyl alcohol (Merck), Polyvinyl pyrrolidone(PVP), Polyethylene glycol (PEG), Ethanol (water free), Potassium Iodide(KI), Iodine(I₂) and deionized ionized water were all A.R. grade from SD Fine Chem reagents and all reagents are used without further treatment before using.

Methods

Synthesis of nano Titanium Oxide

The nano TiO₂ oxide was prepared in the form of a sol-gel by the hydrolysis process. A requisite amount of Titanium (IV) isopropoxide (TTIP) was slowly added in propanol drop by drop. Deionised water is added slowly under stirring for 10 minutes. Then concentrated Nitric acid was used to adjust the pH during the hydrolysis process in the solution. The solution was vigorously stirred for 30 min in order to form sols. After aging for 24 hrs, the sols were transformed into gels. In order to obtain nanoparticles, the gels were dried under 120°C for 2 hr to evaporate water and organic material to the maximum extent. Then the dry gel was sintered at 450°C for 2hrs were subsequently carried out to obtain desired TiO₂ nanocrystalline.

Synthesis of Polymer electrolyte

The preparation of polymer blend electrolyte (PVP/PEG/KI/I₂) by blending technique was reported in earlier literature by Jaisankar et al [10].

Synthesis of Polymer nanocomposite electrolyte

The polymer nanocomposite electrolyte was prepared using solution casting technique. To the above prepared polymer electrolyte, 10 wt% of synthesized nano TiO₂ was dispersed in the viscous gel using ethanol as a solvent. The viscous gel was stirred for 6 hours at 60-65°C in a sealed vessel to obtain a homogeneous solution. The resulting solution was poured into Teflon Petri dish and dried at 50°C for 24 h to remove all traces of solvent. The dried films were peeled off from the Petri-dish and then stored in desiccator to prevent them from any contamination.

Characterisation

The prepared nano TiO₂, polymer electrolyte and polymer nanocomposite electrolyte were characterized using FTIR, XRD and SEM. IR spectra of the n-TiO₂, polymer electrolyte, polymer nanocomposite electrolyte were recorded using a Perkin Elmer IR spectrometer in the range of 400 to 4500 cm⁻¹. The samples were embedded in KBr pellets. The average crystallite size of sample was determined by Debye Scherrer's formula: $D = 0.9\lambda / \beta \cos \theta$ Where X-ray wavelength (1.5406 Å), β full wavelength at half maximum and θ is half diffraction angle. X-ray diffractogram (XRD) is recorded with the help of a Shimadzu diffractometer at a scan rate of 1° /min in the range of $2\theta = 10$ to 80°. The structure and morphology of the n-TiO₂, polymer electrolyte, polymer nanocomposite electrolyte were studied using a HITACHI S-3000 scanning electron microscope (SEM). The electrical conductivity of polymer blend electrolyte and polymer nanocomposite electrolyte were measured by electrochemical impedance spectroscopy. The conductivity (σ) was determined using the relation: $\sigma = t / R_b A$ where t is the thickness of the electrolyte, A , the electrode contact area and R_b is the bulk resistance.

Results and discussion

Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectrum of Nano TiO₂ is shown in the **Figure 1(a)**. It can be observed apparently that strong band in the range of 520 to 550cm⁻¹ is associated with the characteristic modes of TiO₂. The peaks observed at 1450 cm⁻¹ shows

stretching vibrations of Ti-O-Ti. And the peaks around 3400cm^{-1} indicates that the presence of stretching vibration of hydroxyl group of water, which is probably due to the fact that the spectra were recorded in situ and some readsorption of water from the ambient atmosphere has occurred [11]. The peaks around 1630cm^{-1} may be related to bending vibration of hydroxyl groups of molecular water [12]. Figure 1(b) shows the important vibrations detected in the spectrum of PVP/PEG polymer blend. The vibration band of C=O group appears at 1664cm^{-1} of PVP and the C-H stretching at 2887cm^{-1} and the C-O-C (ether) stretching at 1112cm^{-1} of PEG. A very broad band was also visible at 3400cm^{-1} , which was attributed to the presence of water.

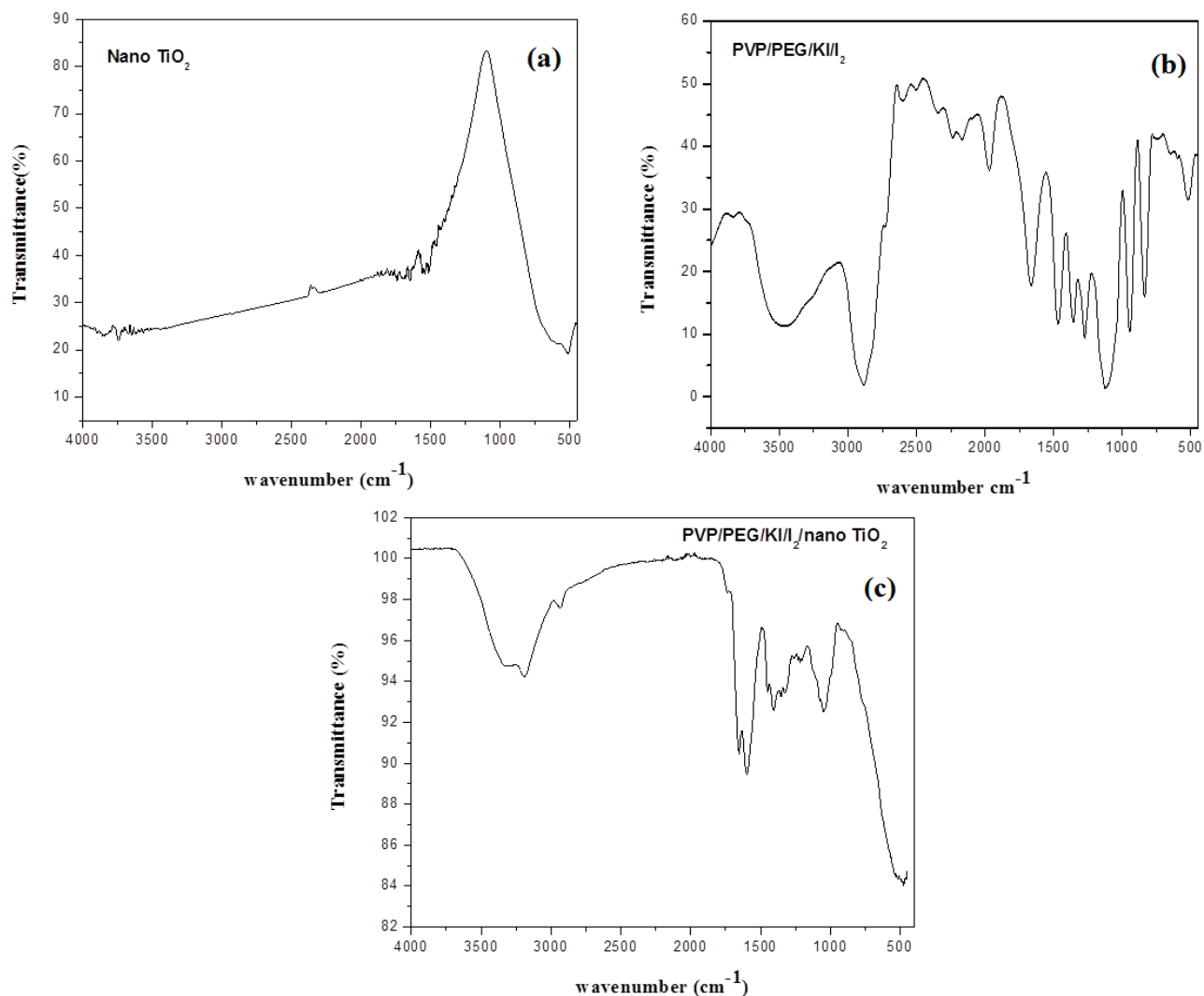


Figure 1 FTIR spectra of (a) nano TiO₂ (b) PVP/PEG/KI/I₂ (c) PVP/PEG/KI/I₂/ nano TiO₂.

Figure 1(c) gives information about the polymer nanocomposite electrolyte in which the nano-filler is added, the peaks of IR spectrum is found to be quite broadened as compared to that of PVP/PEG polymer electrolyte. The vibration peaks at 2887 , 1664 and 1112cm^{-1} is shifted to 2917 , 1606 and 1056cm^{-1} but with decreased peak intensity. It also observed that there is shift in the stretching vibration of TiO₂ to 1420cm^{-1} and the characteristic mode to 480cm^{-1} . The presence of these peaks reveals that the nano TiO₂ is well dispersed with the polymer electrolyte and forms the polymer nanocomposite electrolyte.

X-ray Diffraction analysis

The 2θ scans were recorded at several resolutions using Cu K α radiation of wavelength 1.5406Å range $10\text{-}80^\circ$. **Figure 2(a)** shows the Powder X-Ray Diffraction patterns of the as prepared TiO₂ showed the presence of broad peaks. The broad peaks indicate either particles of very small crystalline size, or particles are semi crystalline in

nature [13]. All the diffraction lines are assigned to anatase crystalline phase of titanium dioxide. From Powder X-Ray Diffraction results, the crystallite size can be estimated from width of the peak through use of Scherrer equation: $D = K \lambda / \beta \cos \theta$, where D is the crystallite size, λ is the wavelength of X-ray radiation ($\text{Cu K}\alpha^{-1}$ radiation = 1.54060 Å), K is a constant and usually taken as 0.9, β is the full width at half maximum (FWHM) after subtraction of equipment broadening, and θ is the Bragg angle of the peak [14]. The prepared nano TiO_2 corresponds to the typical anatase titania crystal and the diffraction data were in good agreement with JCPDS files # 21-1272 structure with peaks at 2θ of 27.3, 36.4, 47.8, 54.7, 56.0, 62.4, 69.2, 70.71 and 74.9 corresponding to (101), (004), (200), (105), (211), (204), (116), (220) and (215) phases respectively [15]. From the Powder XRD spectrum the average crystallite size of nano TiO_2 by sol gel method is found to be 5 nm.

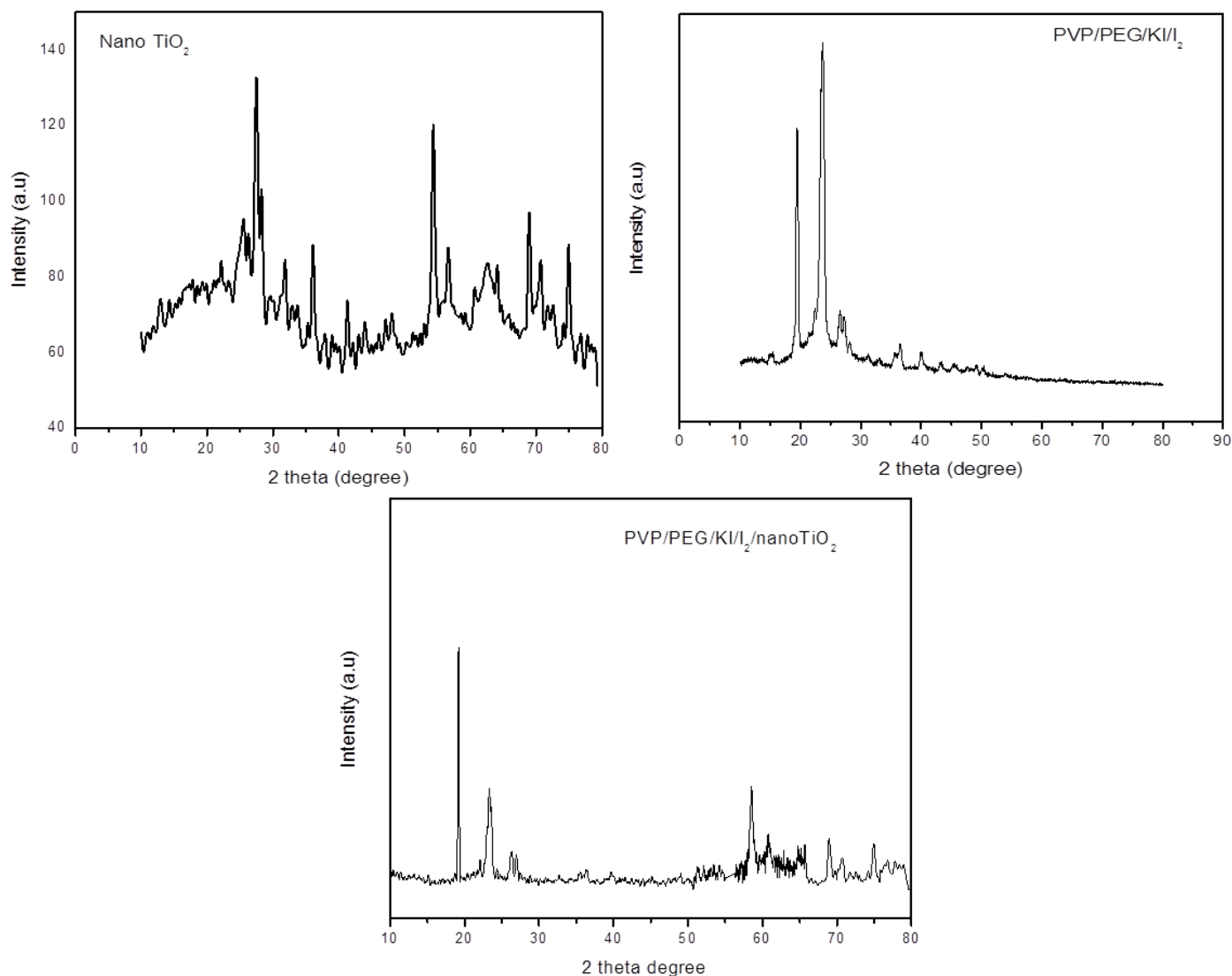


Figure 2 XRD spectra of (a) nano TiO_2 (b) PVP/PEG/KI/I₂ (c) PVP/PEG/KI/I₂/ nano TiO_2 .

Figure 2(b) shows the diffraction spectra of pure PVP/PEG polymer blend. The two prominent peaks of PEG (at $2\theta = 21.6^\circ$ and at $2\theta = 26.45^\circ$) show the crystalline nature of polymer but the spectrum of PVP was characterized by the complete absence of any diffraction peak, which is characteristic of an amorphous compound. None of the peaks corresponding to KI and I₂ salt is found in the composite membrane indicating that the salt is well solvated by the constituents of the membrane. Figure 2(c) shows that nano TiO_2 is dispersed well in polymer electrolyte. The diffraction patterns of polymer nanocomposite electrolyte show a decrease in crystallinity than the pure polymer which is desirable property of the polymer electrolytes. Some of the peaks are disappeared in this spectrum indicates the complete dissolution of nano TiO_2 in the polymer matrix.

Scanning Electron Microscopy (SEM)

The morphology of calcinated titania powders at 450 °C observed by SEM is shown in **Figure 3(a)**. The pure TiO₂ particles exhibited irregular morphology due to the agglomeration of primary particles and with an average diameter of ~6nm.

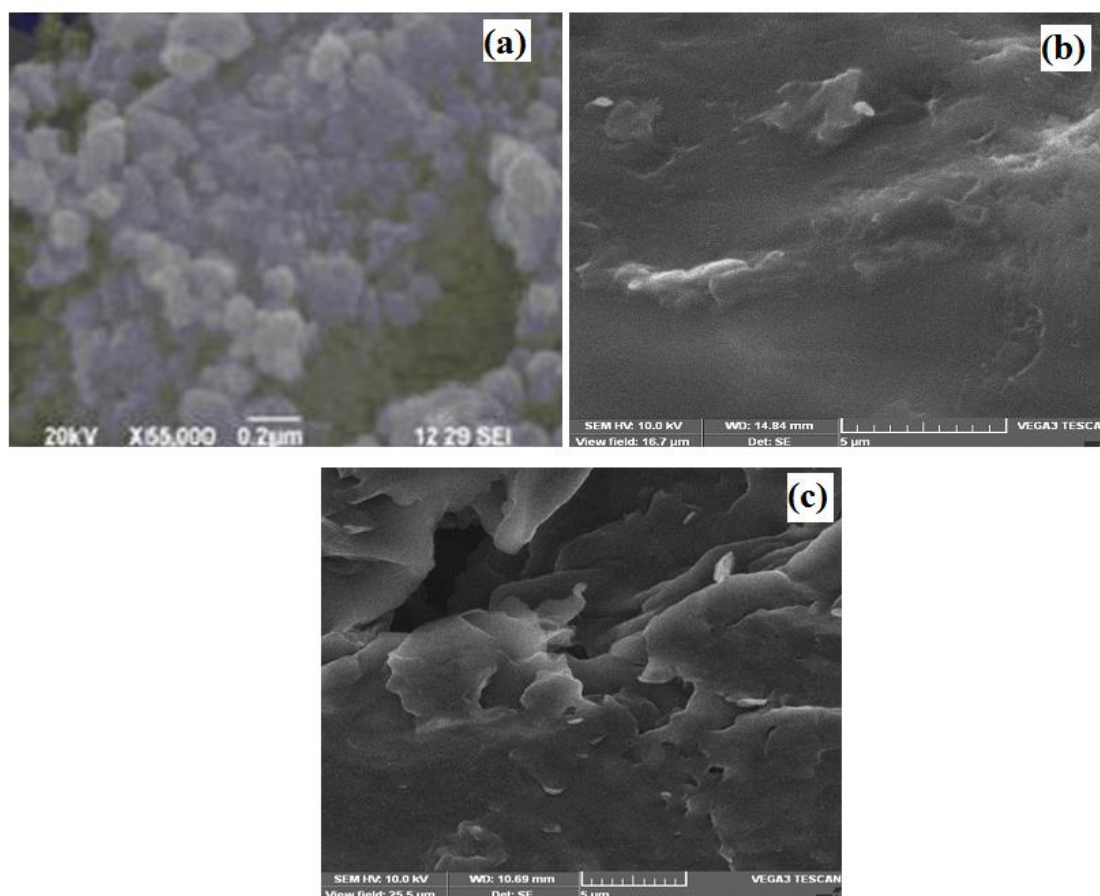


Figure 3 SEM images of (a) nano TiO₂ (b) PVP/PEG/KI/I₂ (c) PVP/PEG/KI/I₂/ nano TiO₂.

Figure 3(b) shows that the addition of PVP to the PEG acts as a plasticizer and enhances the amorphous nature of the polymer. Figure 3(c) shows micrograph with the addition of nano-filler TiO₂, the surface shows a uniformly distributed area. The micro-structural observation is in good agreement with XRD results which have indicated an enhancement in the amorphous phase with the addition of nano-filler.

Conductivity Study

The ionic conductivity of PVP/PEG/KI/I₂ is earlier reported by Jaisankar et al [10] and PVP/PEG/KI/I₂/ nano TiO₂ was calculated using impedance plots 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.

Table 1 Summary of Ionic Conductivity of Polymer Electrolytes.

S.No	Polymer Electrolyte	Ionic Conductivity (S cm ⁻¹)
1	PVP/PEG/KI/I ₂	1×10^{-7}
2	PVP/PEG/KI/I ₂ /nano TiO ₂	4.5×10^{-6}

Table 1 gives the ionic conductivity of polymer electrolyte and the addition of nano TiO₂ to the polymer electrolyte system. It is observed that the addition of nano TiO₂ shows 10 times greater ionic conductivity than that of polymer system. The increase in conductivity is associated with the creation of free ions as a result of addition of filler into the polymer nanocomposite electrolyte.

Conclusion

The polymer gel nanocomposite electrolyte was prepared by solution casting technique. The filler nanoTiO₂ was prepared by sol gel technique. FTIR results revealed that the nanofiller TiO₂ is dispersed in the polymer blend electrolyte. The average size of the particle is calculated using Debye Scherrer's formula and found to be 5 nm and SEM images show that the average diameter of the nano TiO₂ is ~6 nm. XRD results of nano TiO₂ is well fitted with the SEM images of TiO₂. The ionic conductivity of polymer nanocomposite electrolyte (PVP/PEG/KI/I₂/nano TiO₂) is enhanced due to addition of nanofiller as free ions into the polymer system. Thus such polymer nanocomposite electrolyte system finds many application in electrochemical devices such as batteries, fuel cells, electrochromic windows, dye sensitized solar cells and supercapacitors.

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