

EFFECT OF TiO₂ NANOFILLER ON OPTICAL AND IONIC CONDUCTIVITY STUDIES OF (1-X) PVP: X (CH₃COOK) POLYMER ELECTROLYTE FILMS

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ABSTRACT

Nanocomposite solid polymer electrolyte films were prepared by doping TiO₂ nanofiller with different wt% compositions of PVP-CH₃COOK by solution cast technique. Optical absorption studies were performed in the wavelength region 200-800 nm. The energy bandgap values of direct and indirect transitions have been measured and their values were found to be decreasing with increasing wt% of salt. DC ionic conductivity measurements of the prepared nanocomposite films were performed by lab made conductivity four-probe method. The maximum ionic conductivity was found to be 2.01×10^{-3} S/cm at 373 K of the prepared composition 60PVP:40 CH₃COOK: TiO₂ (1 wt %). Transference number of ions and electrons were calculated by Wagner's polarization technique. By using the prepared nanocomposite polymer films, a battery with different wt% ratios has been fabricated and the discharge performance of the cells was presented in this investigation.

Keywords: Nanocomposite polymer electrolyte films, Solution cast technique, UV-visible, Ionic conductivity, Transport properties and Discharge studies.

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INTRODUCTION

Form the past few decades nanocomposite based solid polymer electrolytes were used in many applications such as primary and secondary batteries, grid storage devices, capacitors, energy storage devices and sensors, due to their physical and chemical properties. The first report on polymer electrolyte material has been given by Wright and Armand in 1970s which have taken a growth step towards a new area of research called polymer electrolytes. In general, nanofiller based polymer electrolytes offer higher ionic conductivity over liquid counterparts. Because liquid electrolytes have a lot of disadvantages like leakage problem, rust formation at electrodes, production of gases on overcharging and even explode. To reduce these problems researchers have introduced solid polymer electrolytes which lead to a new path towards energy storage technology¹⁻³.

In recent years scientists have made an effort to develop potassium based solid polymer electrolytes, because potassium has similar behavior like lithium metal. Moreover, potassium is cheaper than lithium and it is freely available from earth crust, which makes the potassium metal as anode material^{4,5}. The mechanical integrity of the polymer electrolytes can be improved by the addition of inorganic fillers like SiO₂, TiO₂, ZrO₂ and Al₂O₃ and also some plasticizers like ethylene carbonate (EC) and propylene carbonate (PC). The nanocomposite polymer electrolyte films which are incorporated with the various alkali metals and plasticizers can act as transits for the drifting of ions through the host polymer matrix. In the present investigation, polyvinyl pyrrolidone (PVP) was chosen as the host polymer because of its excellent physical and mechanical properties. PVP is widely studied by the scientists and has been used in many applications due to its excellent potential performance^{6,7}. Inorganic salt like potassium acetate is used as the dopant material in the preparation of these films. Whereas TiO₂ used nanofiller in order to

improve the mechanical integrity and softness of the films. Rao et al. published their results on different materials in the earlier studies⁸⁻⁵⁵.

EXPERIMENTAL

PVP with average molecular weight (M.W: 36,000), potassium acetate (CH₃COOK) 98% pure and titanium oxide (TiO₂) were purchased from Sigma Aldrich chemicals, India. All the samples were taken in different wt% ratios. The triple distilled water was used as a solvent. The above-mentioned chemicals were placed in a conical flask and kept at continuous stirring for 24 Hrs for complete dissolution. Later TiO₂ (x=1%) was added to get a fine dispersion in the composite polymer solution. After that, the solution was poured into polypropylene petridishes and kept in a hot air oven at 60 °C for 48 hrs to evaporate the solvent. The prepared films were kept in a vacuum desiccator to remove the moisture traces on the prepared films. A set of nanocomposite polymer electrolyte films were prepared with different wt% ratios visually [PVP: CH₃COOK:TiO₂]- (90:10:1%), (80:20:1%), (70:30:1%) and (60:40:1%).

RESULTS AND DISCUSSION

Optical absorption studies

Optical absorption spectra of the prepared nanocomposite polymer films at different wt% ratios of PVP: CH₃COOK:TiO₂ were studied in the wavelength ranging from 200 to 800nm shown in Figure-1(a). It was observed from the spectra that the optical absorption of all the films seems to be decreased with increasing of wavelength. The decrement in the wavelength region was due to the effect of dopant inorganic salt and TiO₂ wt% concentration. An excitation peak has been observed in the optical absorption spectra at 342 nm. This may be due to the titanium nanoparticles dispersed in the polymer chains where the clusters were formed between the ions and polymer matrix^{56,57}. The optical absorption coefficient of the prepared nanocomposite polymer films at different wt% ratios of PVP-CH₃COOK-TiO₂ was shown in Figure-1(b). In the transmission region, an electron is excited from ground energy level to higher energy level and this phenomenon leads to optical absorption process.

From the Figure-1(b), it was clearly observed that as the wt% of salt composition increases in the host polymer matrix, the absorption values were decreased. This change may be due to the cluster bond formation between the salt ions and the polymer chains and also doping of nanofiller affect the decrement of transmitting radiation. At shorter wavelengths, the electrons will be excited to the high energy state and occupy in the vacant positions of energy bands^{58,59}. Thus the energy values were decreased.

Optical absorption coefficient ' α ' is calculated by the following equation,

$$\alpha = 2.303(A/t) \quad (1)$$

Where 'A' is the absorbance and 't' is the thickness of the film

During the transmission radiation, the excitation of electrons in the valence band is equal to the excitation of electrons in the conduction band, due to the insufficient energies at low energy levels (direct bandgap), whereas at higher energy levels (indirect bandgap) the excitation of electrons in the valence band is not equal to the excitation of electrons at the conduction band⁶⁰⁻⁶². The absorption coefficient values can be determined by plotting a graph between α and $h\nu$. From the graph it is evident that as the wt% of salt composition increases in the host polymer matrix by doping with nanofiller, the absorption coefficient decreases and the values are seen at 4.41, 4.32, 4.25, 4.00 and 3.55 eV.

Direct bandgap transitions is calculated by the following relation,

$$\alpha h\nu = C (h\nu - E_g)^{1/2} \quad (2)$$

Where E_g is the energy bandgap, C is a constant value.

Direct bandgap values are obtained from the graph by plotting $(\alpha h\nu)^2$ vs $h\nu$ and the values are at 4.31, 4.21, 4.19, 4.11 and 3.95 eV as shown in Figure.-1(c).

Indirect energy bandgap values can be calculated by the following relation,

$$\alpha h\nu = A (h\nu - E_g - E_p)^2 + B (h\nu - E_g - E_p) \quad (3)$$

Where A and B are constants. Indirect bandgap values are obtained from the graph by plotting $(\alpha h\nu)^{1/2}$ vs $h\nu$ as shown in Figure-1(d) and the values are at 3.81, 3.78, 3.75, 3.41 and 3.22 eV, respectively.

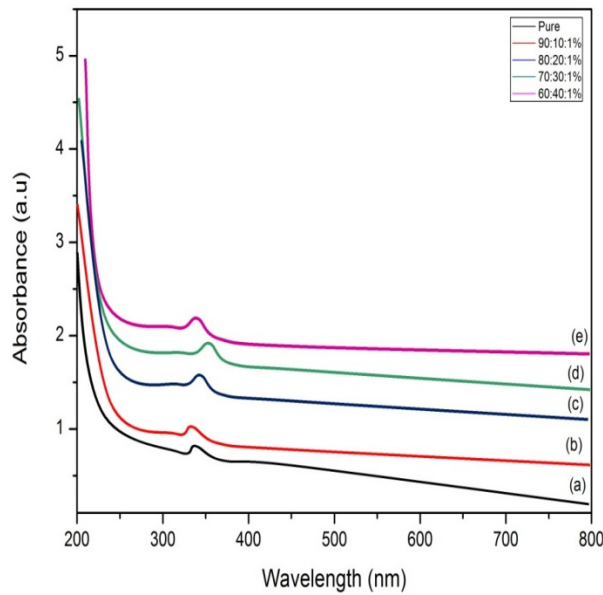


Fig.-1(a): Optical absorption spectra of polymer electrolyte films

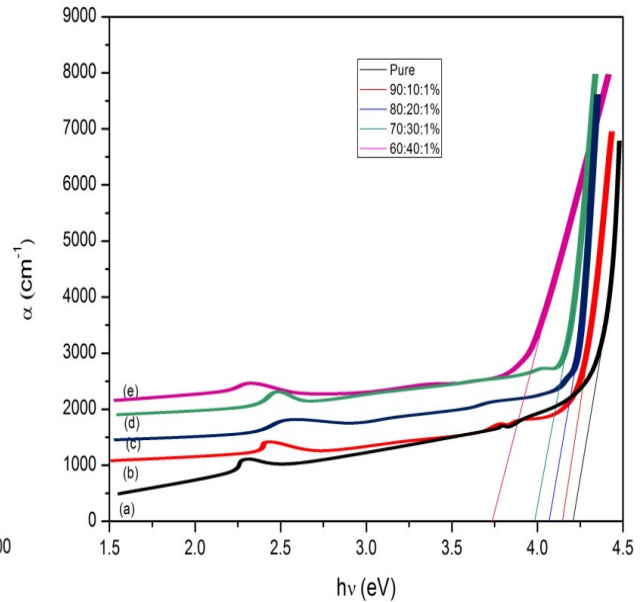


Fig.-1(b): Optical absorption coefficient of nanocomposite solid polymer electrolyte films

From the direct and indirect bandgap values, the optical absorption energy values are found to decrease continuously while doping TiO_2 with PVA + CH_3COOK at different wt% concentrations.

The nanocomposite polymer electrolyte films were prepared at different wt% ratios (90:10), (80:20), (70:30), (60:40) [(1-x) PVA + CH_3COOK] by doping TiO_2 (x%) nanocomposite which act as effective plasticizer to enhance the ionic conductivity⁶³. Among all the obtained energy bandgap values, the wt% ratio (60:40:1%) has the lowest bandgap value which clearly indicates the enhancement of the ionic conductivity. These results agree to the obtained DC conductivity values in the present work.

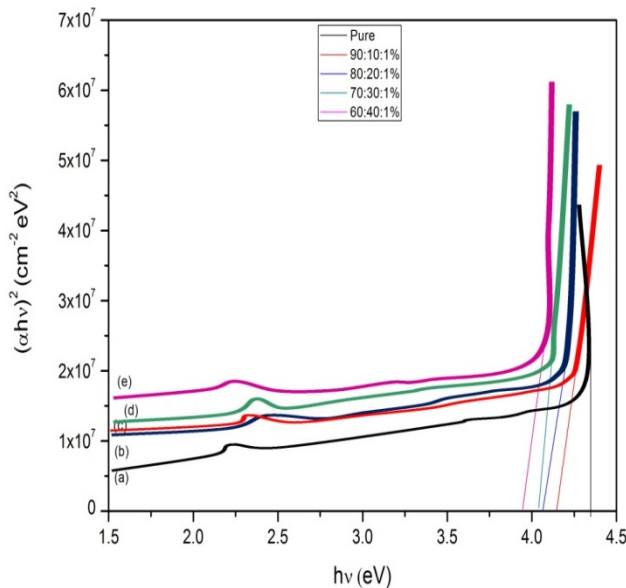


Fig.-1(c): $(\alpha h\nu)^2$ vs $h\nu$ spectra of nanocomposite solid polymer electrolyte films

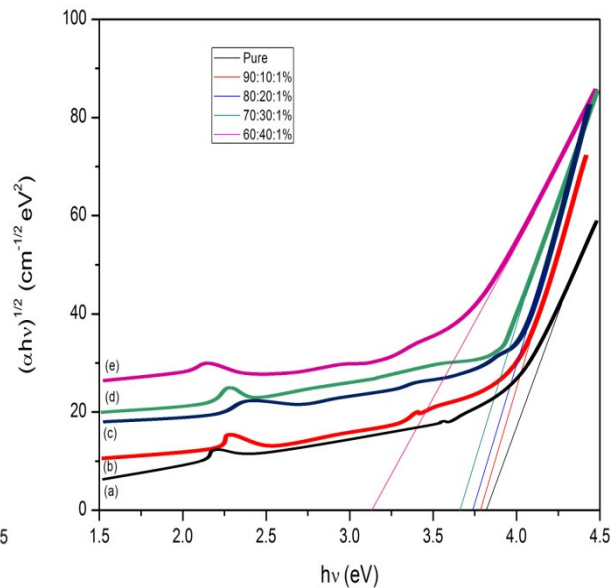


Fig.-1(d): $(\alpha h\nu)^{1/2}$ vs $h\nu$ spectra of nanocomposite solid polymer electrolyte films

D.C. Conductivity studies

DC conductivity measurements of the prepared nanocomposite polymer electrolytes were performed by using lab-made conductivity four probe method while employing Keithley electrometer model 6514. The DC ionic conductivity of the prepared polymer electrolytes was shown in Fig.-2.

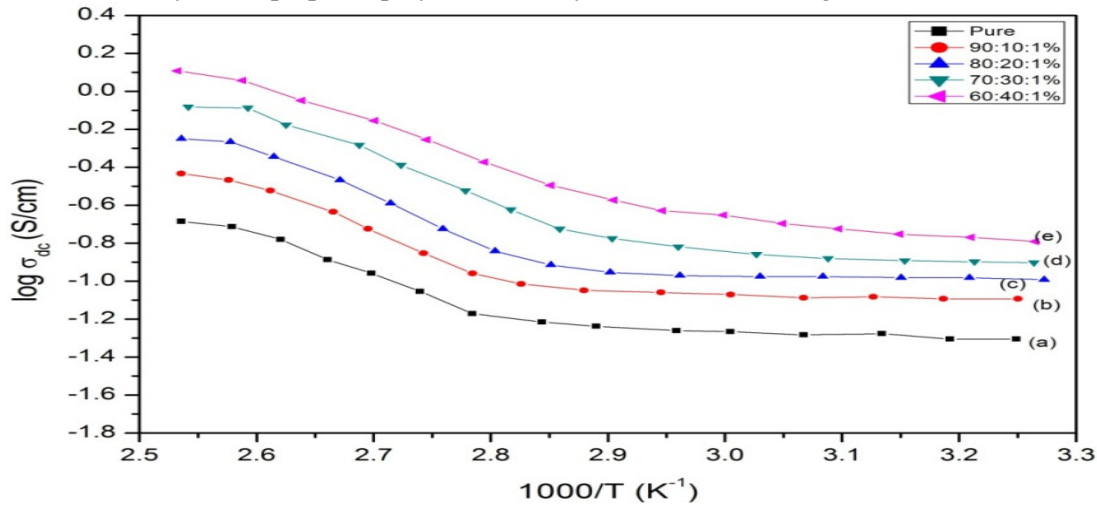


Fig.-2: DC conductivity studies of nanocomposite polymer electrolytes

The conductivity of pure PVP was found to be $1.02 \times 10^{-9} \text{ Scm}^{-1}$ at room temperature. While increasing the temperature, the increase in conductivity has been observed up to $1.13 \times 10^{-5} \text{ Scm}^{-1}$ at 373 K. For the TiO_2 doped polymer electrolytes the ionic conductivity is higher when compared to the pure polymer electrolyte and it was found to be $2.01 \times 10^{-3} \text{ S/cm}$ at 373 K. The obtained values showed the enhancement of ionic conductivity which is higher for TiO_2 doped nanofiller polymer film. The conductivity is calculated by the following relation,

$$\sigma_{dc} = (i \cdot l) / (V \cdot A) \tag{4}$$

Where, *i* is the current,

l is the thickness of the film,

V is the applied voltage,

A is the area of the cross-section of the film.

It is observed from the Figure-2, as increasing the temperature the ionic conductivity is increased linearly up to a certain point and there is a sudden abrupt change occurred. This change may be due to the thermal behavior of the polymer^{64,65}. At this point the semicrystalline phase is converted into amorphous phase; due to the segmental motion of ions and the conductivity in the films has been raised. The calculated DC ionic conductivity values were shown in Table-1.

Transference number

Transport property is defined as the ratio of transference number of any particle/ion to total conductivity (σ_T). The transport properties have been calculated by the following equations using Wagner’s polarization technique and were presented in Table-1.

The total conductivity is given by: $\sigma_T = \frac{\sigma_{ion} + \sigma_{ele}}{\sigma_{hole}}$ (5)

The ionic transference number is given by:

$$t_{ion} = \frac{\sigma_{ion}}{\sigma_T} \tag{6}$$

and the electronic transference number is given by:

$$t_{ele} = \frac{\sigma_{ele}}{\sigma_T} \tag{7}$$

Among the TiO₂ doped ratios of [(1-x)PVP]+(x) CH₃COOK polymer electrolyte films, the sample with 60:40:1% wt% ratio has the high transfer of ions and it was found to be 0.99. The current with respect to time plot was shown in Figure.-3.

Table-1: Conductivity and transference numbers of (PVP: CH₃COOK: TiO₂) electrolyte system

Nanocomposite polymer films	Conductivity at RT (Scm ⁻¹)	Conductivity at 373 K (Scm ⁻¹)	Transference number	
			t _{ion}	t _{ele}
Pure PVP	1.02x10 ⁻⁹	1.13 ×10 ⁻⁵	-----	-----
PVP:CH ₃ COOK:TiO ₂ (90:10:1%)	3.12x10 ⁻⁸	3.10x10 ⁻⁴	0.94	0.06
PVP:CH ₃ COOK:TiO ₂ (80:20:1%)	4.05x10 ⁻⁷	4.15x10 ⁻⁴	0.96	0.04
PVP:CH ₃ COOK:TiO ₂ (70:30:1%)	5.21x10 ⁻⁶	5.10x10 ⁻⁴	0.98	0.02
PVP:CH ₃ COOK:TiO ₂ (60:40:1%)	2.25x10 ⁻⁵	2.01x10 ⁻³	0.99	0.01

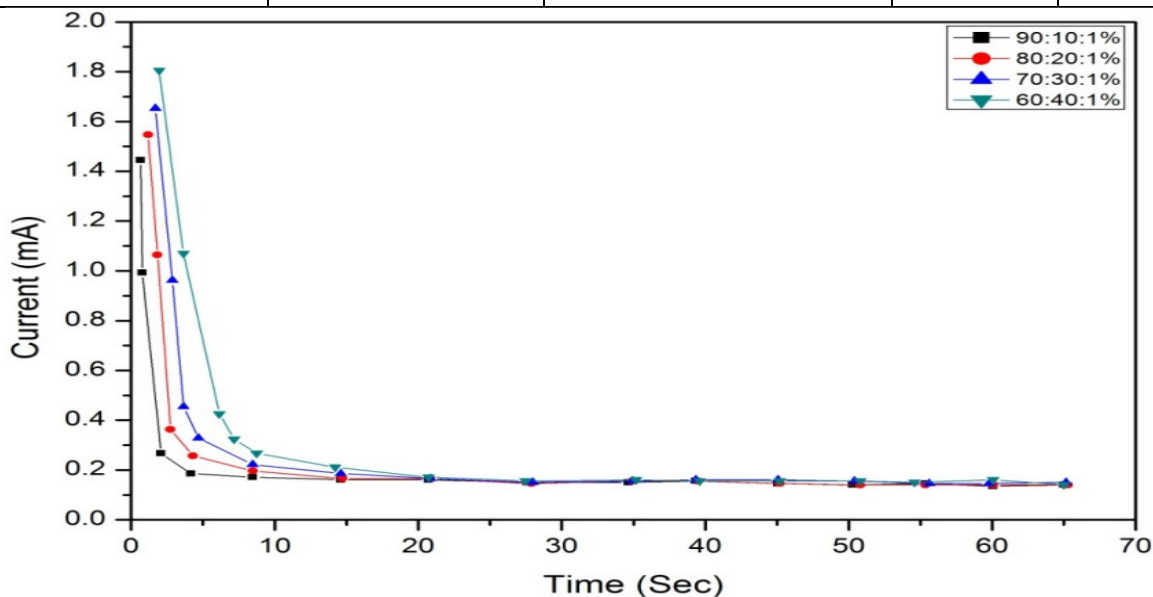


Fig.-3: Transport properties of nanocomposite solid polymer electrolyte films

Initially, polarization and the current (i_t) rises up followed by immediate decay of current and attain steady state after a long time of polarization have been observed. This may be due to the current flow across the cell at the blocking electrode under the influence of an applied voltage⁶⁶. The ionic transference values are obtained in between 0.94-0.99. This clearly shows that among all the wt% ratios of samples the majority transfer of ions 0.99 and minority of electrons 0.01 are found for the sample (60:40:1%).

Discharge Characteristics

TiO₂ doped solid-state polymer battery has been fabricated at room temperature with the configuration of K⁺(anode)/polymer electrolyte/ (I+C+electrolyte)/(cathode). In the anode region due to the potassium metal the charge carrier's takes place and in cathode region due to the mixture of iodine and carbon powder material enhances its electronic conductivity⁶⁷. Figure-4 shows the discharge characteristics of the prepared solid-state battery.

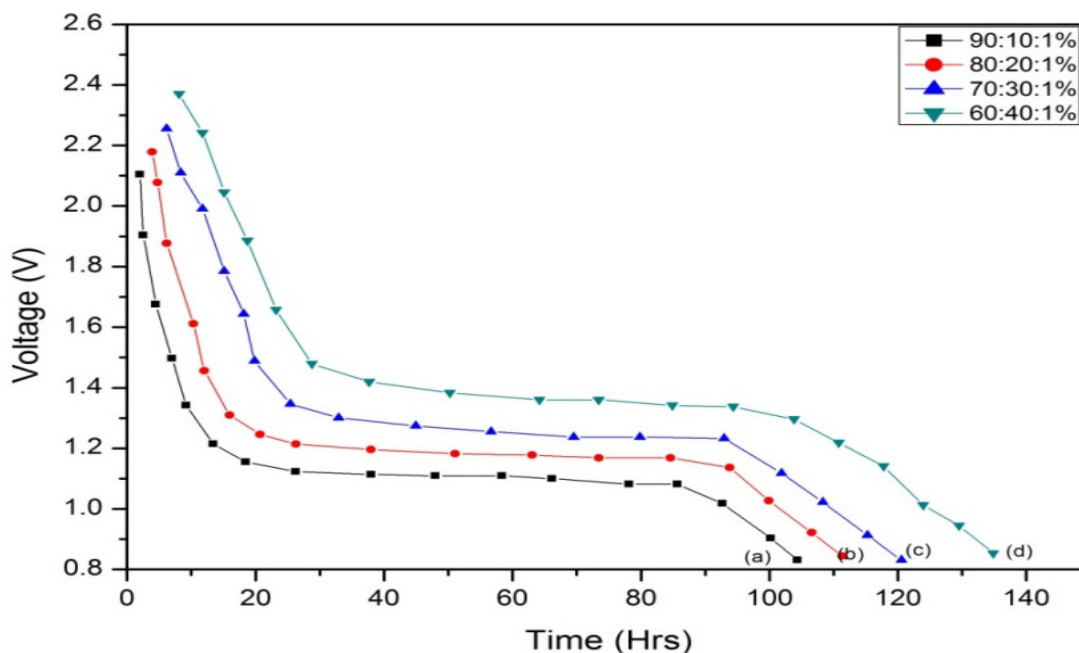


Fig.-4: Discharge characteristics of nanocomposite solid polymer electrolyte films

At first the decrement in the voltage has been observed, this may be due to the polarization of current in an electrolyte and formation of a thin layer of potassium salt between the electrode-electrolyte interfaces. On comparison of all the wt% ratios, the nano-doped polymer battery [PVP: CH₃COOK: TiO₂] (60:40:1%) exhibits better performance and found to have the higher stability up to 136 Hrs than the other polymer batteries.

CONCLUSION

Nanocomposite polymer films have been prepared with different wt% ratios by doping TiO₂ nanofiller to PVP: CH₃COOK by solution cast technique. Optical absorption and energy bandgap values were decreased due to the cluster bond formation between the salt ions and the polymer chains. This may be due to the doping of nanofiller will affect in the decrement of transmitting radiation. From the DC conductivity studies, the ionic conductivity was found to be high 2.01×10^{-3} S/cm at 373 K of the composition 60PVP:40 CH₃COOK: TiO₂ (1 wt %). The Discharge characteristics of the nano-doped polymer battery showed better performance and stability up to 136 Hrs.

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[RJC-2016/2017]