Research Article

Effect of TiO$_2$ Nano-filler on Dielectric Studies of PVP based Solid Polymer Electrolytes

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Abstract
The logarithmic frequency dependent dielectric behavior of solid polymer electrolyte has been prepared with the combination of PVP (polyvinyl pyrrolidone), Magnesium sulphate heptahydrate (MgSO$_4$.7H$_2$O) and TiO$_2$ as nano-filler by solution casting technique. Dielectric studies were performed using AC impedance analyzing technique in the frequency range 42 Hz - 5 MHz. At lower frequency the dielectric studies show the relaxation contribution which is superimposed by the electrode polarization effect. The dielectric constant was found to be increased with increasing the wt% of the sample and the ionic conductivity was higher for 20 wt% MgSO$_4$.7H$_2$O concentration.

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Introduction

The development of polymer electrolyte systems with high ionic conductivity is one of the main objectives in polymer research. This is because of their potential applications as electrolytes in solid-state batteries, fuel cells, electrochemical display devices/smart windows, photo-electrochemical cells etc., [1-3] due to their high conductivity, high energy density, wide electrochemical stability and easy processibility. Intrinsically conducting polymers have attracted the attention of researchers because of their numerous applications [4, 5]. In recent years tremendous effort has been made in the preparation of solid polymer electrolytes. The recent research trends in the field of rechargeable lithium batteries are directed towards the development of cells with high-energy density (wh/kg) and high-power density. A primary work in the field of solid polymer electrolyte has been carried by Wright et al.[6, 7] and found that the ionic conductivity is the order of 10^{-5} S/cm at 330 K in PEO and NaSCN complexes.

A wide range of interest has been focused to prepare solid polymer electrolytes over a few decades due to their potential applications as electrolyte materials in high energy density batteries, rechargeable batteries and solid state batteries [8, 9]. Magnesium is used as the excellent material for anode in solid state batteries which is naturally available in earth crust, in addition magnesium based devices are much cheaper than lithium devices, whereas magnesium is less reactive, non-toxic than the lithium in ambient temperatures and atmospheric conditions. So magnesium is used instead of lithium for solid state battery application [10].

Polyvinyl pyrrolidone (PVP) has played major role in displaying dissolubility, stability, high-dielectric constant and compatibility. PVP is soluble in polar solvents as well as in ionized water and also acts as thermally stable, cross linked with the composites and having high mechanical strength. PVP is chosen because it is having good mechanical, electrical and optical characteristics. Pyrrolidone group of PVP prefers to incorporate with organic and inorganic salts resulting in the formation of film which has good dispersion and surface formation[11]. Solid polymer electrolyte complexed with inorganic salt and nano-fillers/plasticizers was first introduced by Weston and Steele in 1982 [12]. The addition of the fillers in the solid polymer electrolytes improves the electrical and mechanical strengths of the polymer [13]. Rao et al. presented their results in their earlier studies [14-27].

In this present work we have reported that the solid polymer electrolyte films were prepared by adding the TiO$_2$ particles to PVP -MgSO$_4$.7H$_2$O, the content of this work is to enhance and improve the ionic conductivity by comparing with the other polymer electrolytes. The variation of dielectric properties of the prepared polymer

electrolyte samples for different wt% compositions were observed in the present study.A difference in the peak positions were obtained for different compositions, which suggests the presence of relaxing dipoles in the prepared samples.

Experimental
Sample preparation

PVP Sigma Aldrich chemicals based solid polymer electrolyte films doped with pure magnesium sulpahate heptahydrate and TiO_2 nanoparticles were dispersed in different ratios (95:5) (90:10), (85:15) and (80:20) by solution casting technique and double sterilized water is used as a solvent. The mixture of TiO_2 doped in polymer solution was stirred for 24 hours to obtain nanocomposite polymer solutions (NCP's).Later the homogeneoussolution was placed in polypropylene dishes andevaporated slowly at 60 ^{o}C in hot air oven. Later the nano-composite polymer films were peeled off and placed in a desiccator.

Results and Discussion
Cole-Cole Plots

The conductivity plots for PVP: $MgSO_4.7H_2O$ +TiO_2 polymer electrolyte films for various wt% at room temperature (303 K) are shown in **Figure 1**. The analysis of Cole-Cole plot has been measured by applying small amount of AC current across the sample; the variation of imaginary (Z^{II}) and real part (Z^{I}) can be measured by using LCR: HIOKI 3532-50 LCR Heister Range 42 Hz – 5 MHz. Due to the good contacts between electrode-electrolyte interfaces an electrode polarization phenomenon occurs. The Cole-Cole plot is obtained from the real part (Z^{I}) vs an imaginary part (Z^{II}). Nyquist plot (Cole-Cole) generally consists of semi-circular arc at higher frequency and a spike is formed at lower frequency for the bulk resistance. In the obtained plots the spike formation can be seen; it is due to mainly of ionic conduction [28]. The obtained conductivity values are sown in **Table 1**. The AC conductivity can be calculated from the bulk resistance (R_b) which is inter related by equitation

$$\sigma = t/ R_bA \qquad\qquad (1)$$

Where"t" is the thickness of the film, "A" is the area of the film and "Rb" is the bulk resistance.
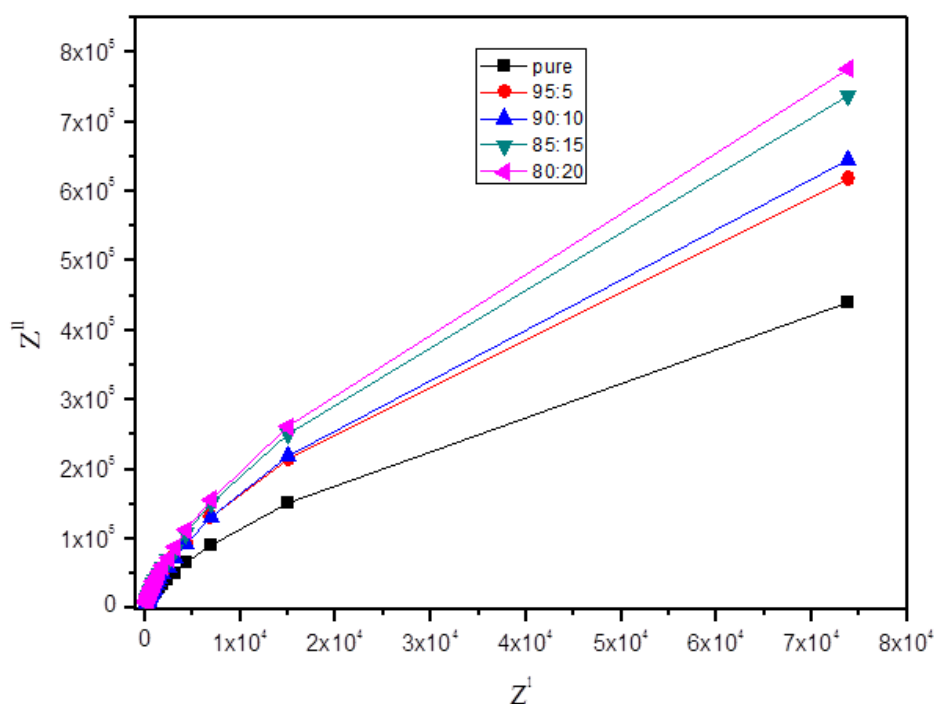

Figure 1 Cole-Cole plots for the PVP: $MgSO_4.7H_2O$+TiO_2 polymer electrolyte films for different wt% at 303K

Table 1 Conductivity of PVP+MgSO$_4$.7H$_2$O solid polymer electrolyte System

AC Conductivity values of (PVP+ MgSO$_4$.7H$_2$O)Polymer electrolytesystem	
Films	Conductivity at room temperature
PurePVP	1.02×10^{-9} (S/cm)
PVP+ MgSO$_4$.7H$_2$O+TiO$_2$(95:5)	2.52×10^{-8} (S/cm)
PVP+ MgSO$_4$.7H$_2$O+TiO$_2$ (90:10)	3.83×10^{-8} (S/cm)
PVP+MgSO$_4$.7H$_2$O+TiO$_2$(85:15)	3.01×10^{-7} (S/cm)
PVP+MgSO$_4$.7H$_2$O+TiO$_2$ (80:20)	1.12×10^{-6} (S/cm)

Dielectric Spectroscopy

The dielectric spectroscopic studies were carried-out by using HIOKI 3532-50 LCR Heister in the frequency range from 42 Hz to 5 MHz at room temperature. The logarithmic frequency of the sample with respect to dielectric constant data was shown in **Figures 2** and **3** which indicates the dielectric constant is a measure of amount of charge stored. As increasing the frequency the dielectric constant values are gradually decreases and found to be high for the sample 20 wt%; this concludes that the drifting of ions is high giving raise to conductivity phenomenon. This reveals that the salt is completely dissolute in the polymer chains giving raise to mobile ions. Due to the formation of space charge region at the electrode and electrolyte interfaces a variation is observed in between dielectric constant of ε^{1} and ε^{11} with increasing frequency; this behavior is known as non–Debye behavior.
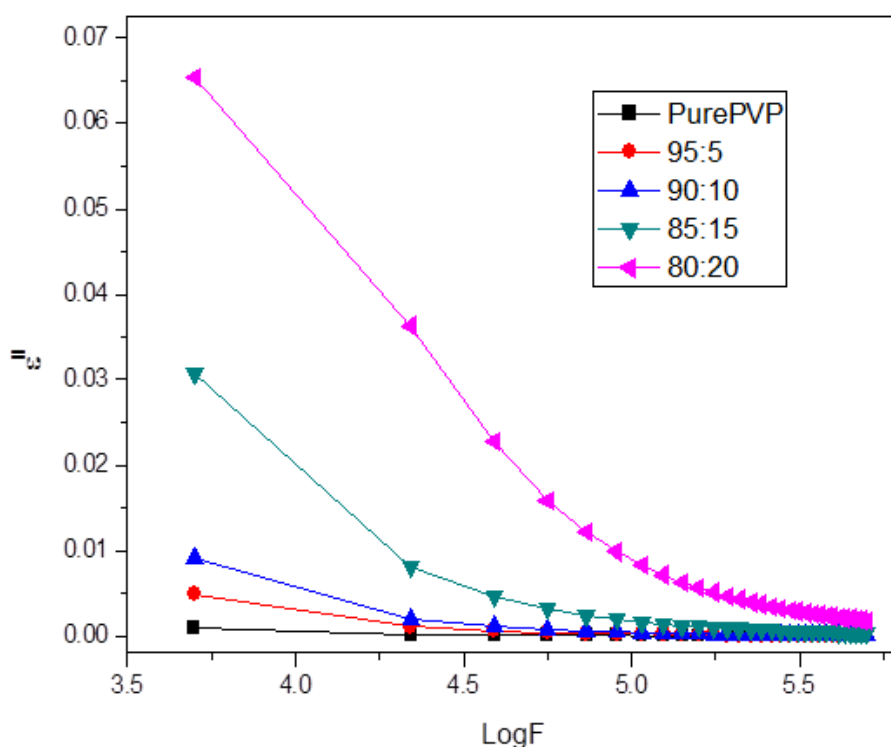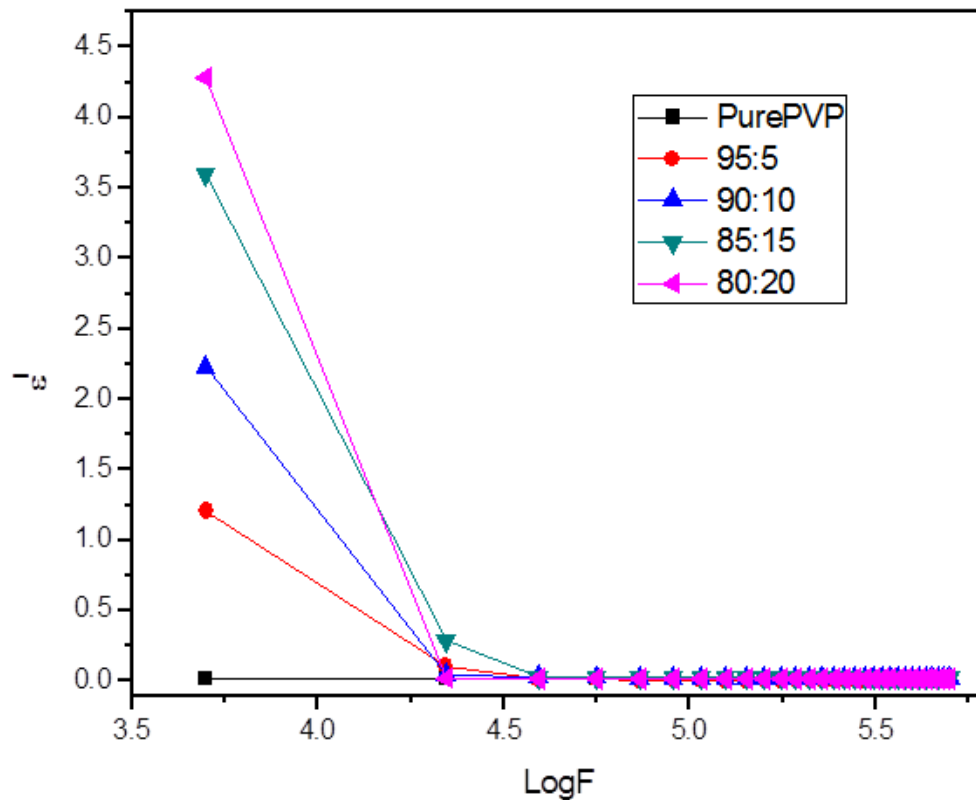

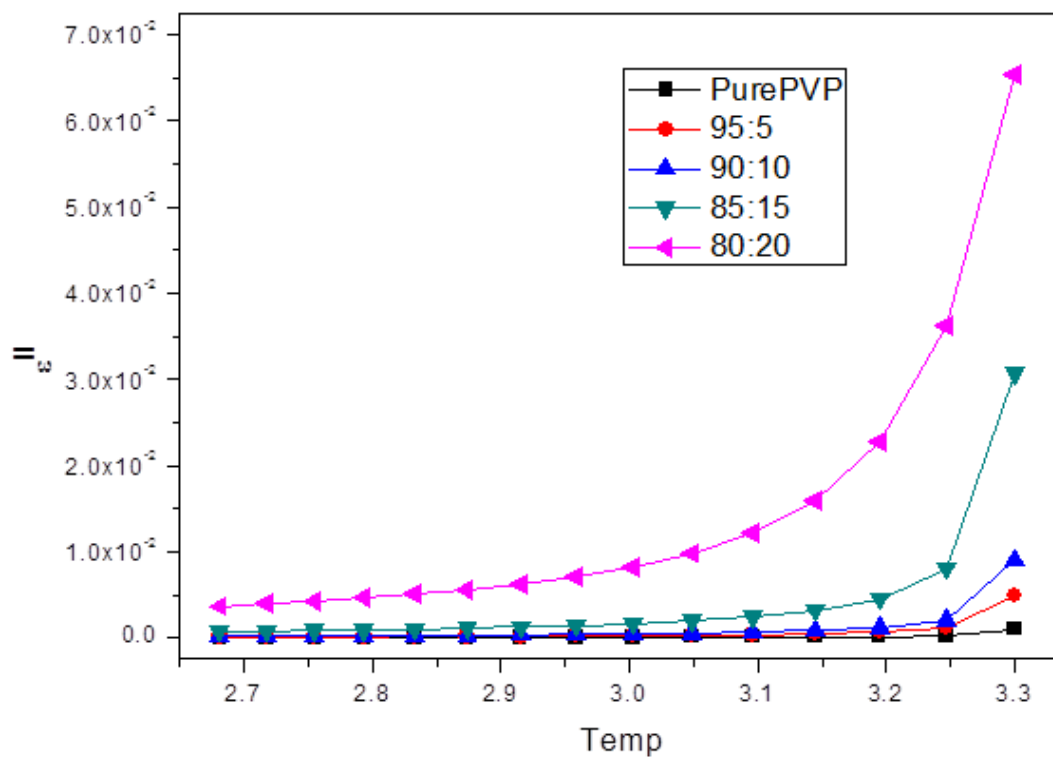**Figure 2** Variation of log F with dielectric permittivity for different wt% at 303 K

The dielectric constant of composite samples as a function of room temperature is shown in **Figure 4**. The dielectric constant of composite polymer electrolytes increases apparently with the increase of temperature. The increment of dielectric constant peak is observed at room temperature. The abrupt change in dielectric constant has been verified by the conductivity. This is due to the ionic jump orientation, space charge polarization and electronic contribution of Mg^{2+} ions [29].

Figure 5shows the variation of dielectric permittivity with the frequency for PVP: MgSO$_4$.7H$_2$O+TiO$_2$, polymer electrolyte at room temperature and observed that as increasing the frequency the dielectric permittivity decreases monotonically and at higher frequency the dielectric constant remains constant and the similar behavior is observed in
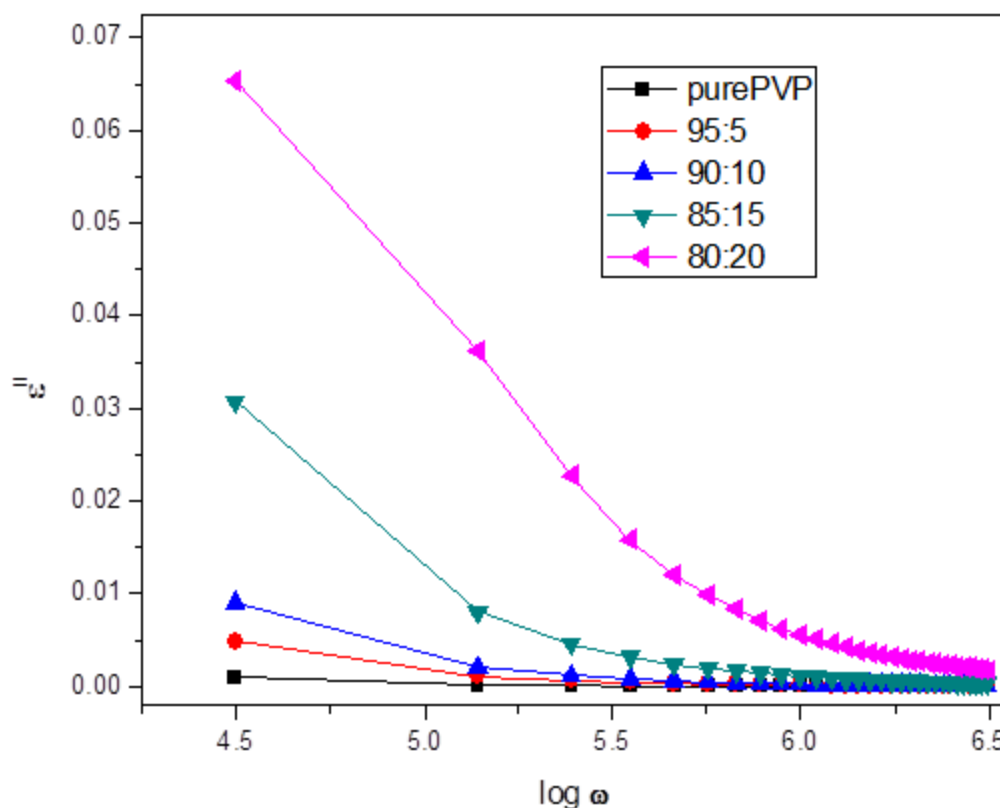
reaming samples, which could be due to the dipole interaction and electrode-electrolyte polarization effects. At higher frequencies, the ionic diffusion doesn't takes place in the direction of the field [30].

Figure 3 Variation of log F with dielectric permittivity for different wt% at 303 K

Figure 4 Variation of temperature with dielectric permittivity for different wt% at 303 K

Figure 5 Variation of dielectric permittivity with the frequency for different wt% at 303 K

Conclusions

Solid state polymer electrolyte of Mg^{2+} was prepared by PVP complexed with $MgSO_4.7H_2O$ and TiO_2 as nano-filler by solution casting technique. From the conductivity studies the higher conductivity for PVP:$MgSO_4.7H_2O$+TiO_2 (80:20) was found to be 1.12×10^{-6} (S/cm) at room temperature. The increase of frequency with the decrease of dielectric permittivity at room temperature and at higher frequency the dielectric constant remains constant, which could be due to the dipole interaction and electrode-electrolyte polarization effects.

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