DC-Ionic Conductivity and Dielectric Studies of PVP-CH₃COOK Based Solid Polymer Electrolyte Films

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Abstract
Solid polymer electrolyte films were prepared with different wt% compositions of PVP-CH₃COOK by solution cast technique. DC ionic conductivity measurements for the prepared nanocomposite films were performed by lab made conductivity four probe method. From the measurements the higher ionic conductivity was found to be 2.31×10^{-5} S/cm at 373 K for the composition 80PVP:20CH₃COOK. Dielectric studies were performed on the prepared polymer films at room temperature in the frequency ranging between 5000 Hz and 50000 KHz to find the best optimum conductivity and electric relaxation process of the samples.

Introduction

Over a past few decades an attractive attention has been made towards nanocomposite materials due to the low production cost and excellent structural, electrical, thermal and magnetic properties [1]. Solid polymer films are expected to exhibit a major change in wide range of technological applications and industrial fields such as conductive coating, humidity sensors, microwave absorbing, energy storage devices and fuel cells etc. Solid polymer films are prepared by doping inorganic salt in the host polymer. The mechanism of solid polymer electrolytes and the advantages were reported by Wright and Armand in 1970s [2, 3]. Due to many advantages solid polymer electrolytes have taken a new development in the field of energy storage devices. The work on these polymer electrolytes has received great attention and leads a new way to the researches in the development of batteries and electrochromic windows basing on the fast ion movement [4].

Polyvinyl pyrrolidone (PVP) polymer has brought a drastic change in both the academic and industrial world ever since it comes to experimental existence [5, 6]. Polyvinyl pyrrolidone has excellent physical and mechanical properties such as high thermal conductivity, good mechanical strength, high specific surface area and large scale screen printing of electrolyte films at low cost and high mobility of charge carriers [7]. PVP is also used in many applications such as batteries, solar cells, fuel cells and super capacitors [8, 9]. Inorganic salt like potassium acetate is used as dopant material to the host polymer in order to enhance the ionic conductivity. Rao et al. presented their results in their earlier studies [10-42]. In the present investigation, solid polymer films were prepared with different wt% composition ratios of PVP-CH₃COOK in order to improve the ionic conductivity and dielectric properties of the composite films.

Experimental
Preparation of Nanocomposite Polymer Films

PVP with average molecular weight (M.W: 36,000), potassium acetate (CH₃COOK) 98% pure 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. After that the solution was poured in polypropylene petridishes and kept in a hot air oven at 60 °C for 48 hrs to evaporate the solvent. A set of PVP-CH₃COOK solid polymer electrolyte films were prepared at different wt% ratios (95:5), (90:10), (85:15) and (80:20). Finally the prepared films were kept in a vacuum desiccator to remove the moisture traces on the prepared films.

Results and Discussion
DC-ionic conductivity

The DC-ionic conductivity of the prepared polymer electrolyte films with different wt% compositional ratios is shown in **Figure 1**.
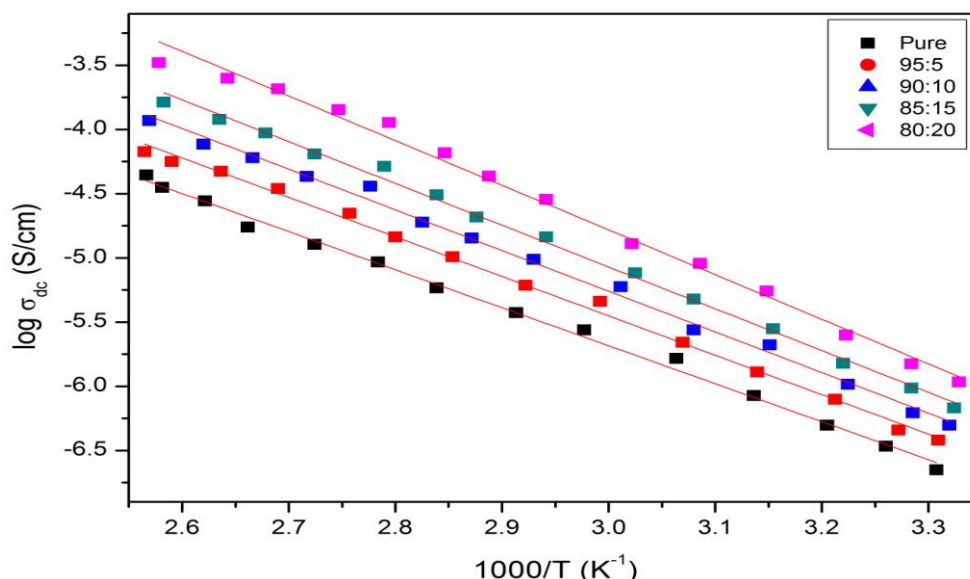
Figure 1 DC-Ionic conductivity of solid polymer electrolyte films

The conductivity of pure PVP is found to be 1.02×10^{-9} Scm^{-1} at room temperature. As increasing the temperature and compared to pure PVP, the conductivity found to be 2.31×10^{-5} S/cm at 373 K for compositional ratio 80PVP:20CH$_3$COOK. From the Figure it is clearly observed that as increasing the temperature the ionic conductivity increases linearly up to a certain point and then there is a sudden abrupt change occurs. This change may be due to the thermal behavior of the polymer [43]. At this point the semicrystalline phase is converted in to amorphous phase which leads to increase in the ionic conductivity. The ionic conductivity was calculated by using the formula,

$$\sigma_{dc} = (i \times l)/(V \times A) \tag{1}$$

Where i is the current, l is the thickness of the film, V is the applied voltage and A is the area of cross section of the film.

The calculated DC ionic conductivity values are shown in **Table 1**.

Table 1 Ionic conductivity of solid polymer electrolytes

| Solid polymer electrolyte films	Conductivity (Scm^{-1})	
	at room temperature	at 373 K
Pure PVP	1.02×10^{-9}	1.13×10^{-8}
PVP:CH$_3$COOK (95:5)	3.12×10^{-8}	3.10×10^{-7}
PVP:CH$_3$COOK (90:10)	4.05×10^{-8}	4.15×10^{-7}
PVP:CH$_3$COOK (85:15)	1.21×10^{-7}	5.10×10^{-6}
PVP:CH$_3$COOK (80:20)	6.25×10^{-7}	2.31×10^{-5}

Dielectric Properties

The real (ε^{l}) and imaginary parts (ε^{11}) of dielectric constant with respect to frequency is shown in **Figure 2**. From the Figures it is clearly observed that the values of real and imaginary parts are continuously decreasing with increase in frequency for a particular time of interval and becomes stabilized due to polarization phenomenon and also observed that the dielectric constant value is found to be high for the sample 80PVP:20 CH$_3$COOK. This may be due to the formation of space charge region at the electrode-electrolyte interfaces [44, 45]. The decrease in dielectric constant is due to the complete miscibility of salt in the host polymer matrix, which in turn the mobilization of ions in the polymer matrix and this leads to the enhancement of electric conductivity [46].

The logarithmic frequency with respect to real (ε^{l}) and imaginary parts (ε^{11}) of dielectric constant is shown in **Figure 3**. From the Figures it is clearly observed that the values of real and imaginary parts are continuously decreasing with increase in the logarithmic frequency and the dielectric values have found to be high for the sample at 20 wt%. This may be due to the mobilization of ions resulting in the formation of electric field at the electrode surfaces [47]. Due to the complete dispersion of salt in the host polymer, the drifting of ions resulting in increase of polarizability at electrodes and is proportional to ωn^{-1}, indicating non-Debye behavior [48].
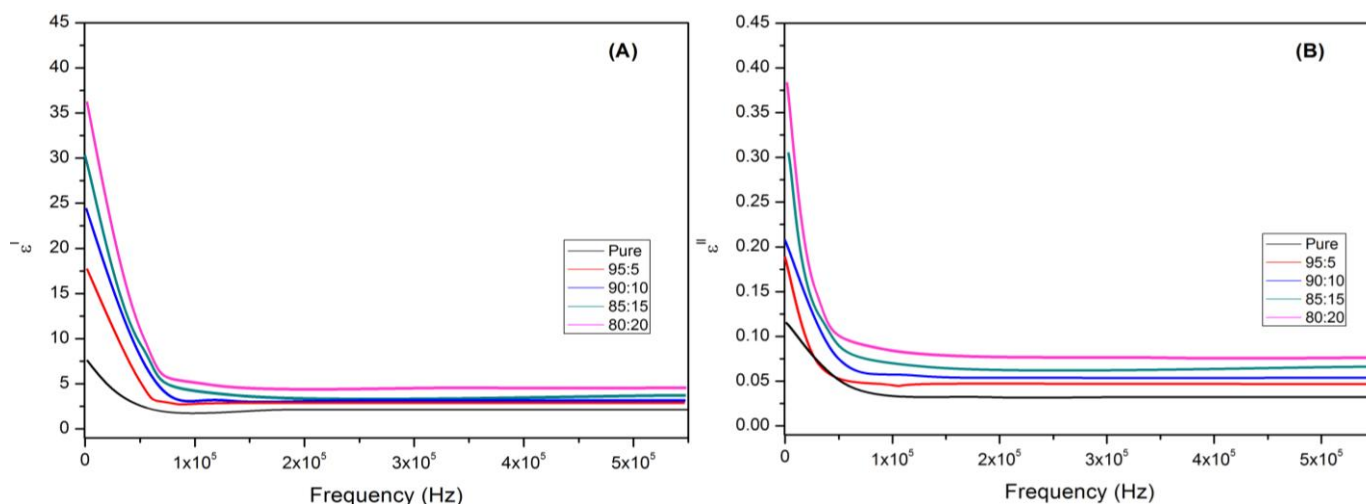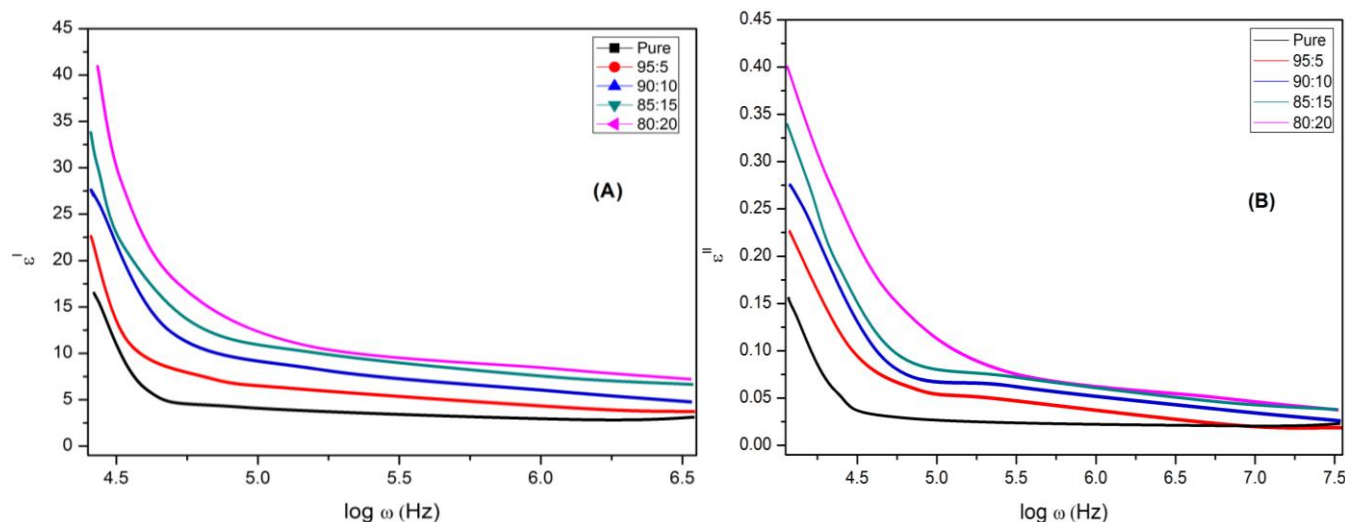

Figure 2 (A) Variation of ε^{l} with frequency for different wt% ratios, (B) Variation of ε^{11} with frequency for different wt% ratios
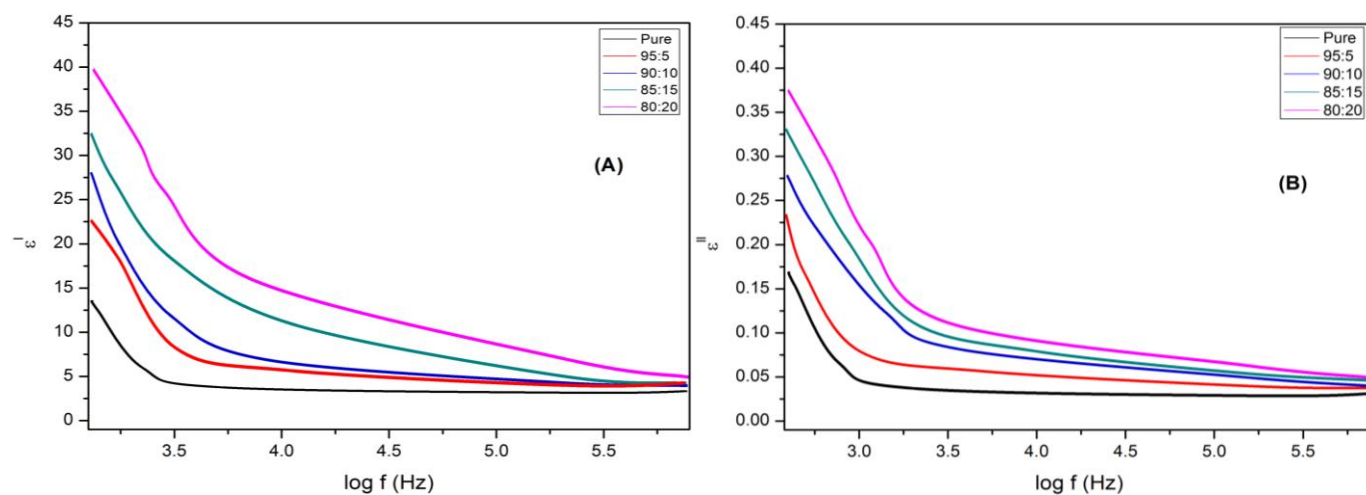

Figure 3 (A) Variation of ε^{l} with logarithmic frequency for different wt% ratios, (B) Variation of ε^{11} with logarithmic frequency for different wt% ratios

The variation of real (ε^{l}) and imaginary parts (ε^{11}) of dielectric constant with respect to logarithmic angular frequency (ω) for different wt% ratios of the polymer electrolyte samples have shown in **Figure 4**. From the Figures the monotonic decrement in dielectric values has been observed with increase in the logarithmic frequency. This may be due to the reduced proportion of amorphous material leading to reduction in the magnitude of dispersion [49]. Similar behavior has been observed in the rest of the samples.

The variation between logarithmic conductivity with respect to the frequency is shown in **Figure 5**. From the Figure it is observed that the ionic conductivity increases as increasing the frequency and the maximum ionic conductivity is found for the compositional ratio 80PVP:20 CH_3COOK. The plateau region describes the space charge polarization at the blocking electrode and is associated with ionic conductivity (σ_{dc}) of the complex nature of polymer electrolyte. However at high frequencies the conductivity variation with temperature is much less than that of lower frequencies. This may be due to large scale heterogeneity of salt particles doped in the host polymer [50].

Figure 4 (A) Variation of ε^1 with logarithmic angular frequency for different wt% ratios, (B) Variation of ε^{11} with logarithmic angular frequency for different wt% ratios
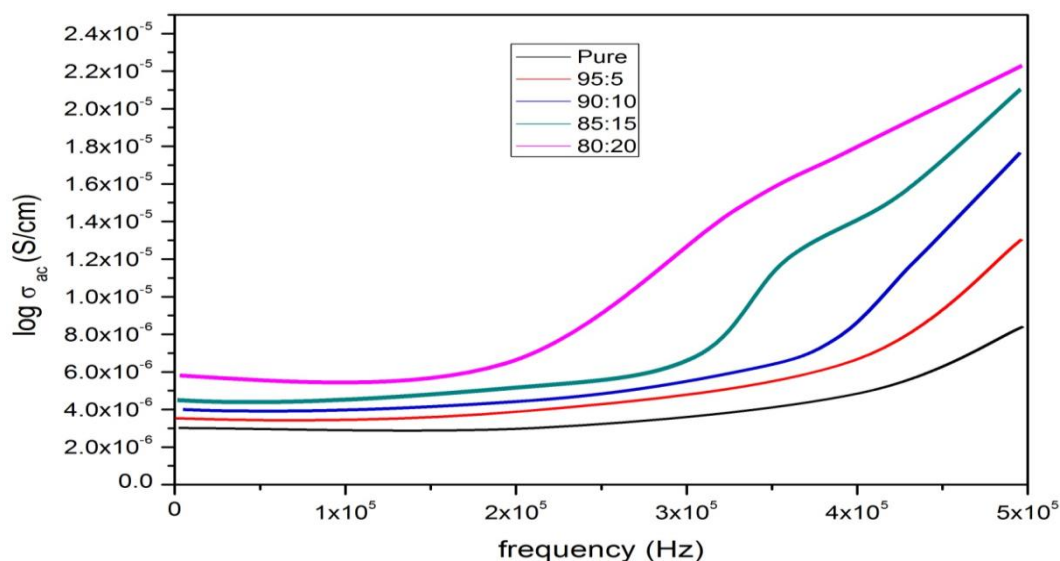
Figure 5 Variation of logarithmic conductivity vs frequency for various wt% ratios

Conclusion

Solid polymer films have been prepared with different wt% ratios of PVP: CH_3COOK by solution cast technique. DC-ionic conductivity measurements showed that the higher ionic conductivity was found to be 2.31×10^{-5} S/cm at 373 K for the composition $80PVP:20CH_3COOK$. Dielectric studies were performed on the prepared solid polymer electrolyte films at room temperature and found that the best optimum conductivity and electric relaxation process exist for the composition $80PVP:20CH_3COOK$.

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