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ARTICLE

AC Impedance and FTIR Studies of PVA-$ZnCl_2$ Based Solid Polymer Electrolytes

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ABSTRACT

Solid Polymer electrolytes (SPEs) comprising of poly(vinyl alcohol) (PVA) added Zinc chloride ($ZnCl_2$) systems have been prepared via solvent casting technique. The prepared samples have been subjected to AC impedance spectroscopic analysis and Fourier Transform Infrared Spectroscopy (FTIR) studies. Maximum ionic conductivity of $3.91949*10^{-7}$ Scm^{-1} was achieved for 60 wt% of PVA and 40wt% of $ZnCl_2$ system at room temperature. The structural changes and hence the complex formation between the constituents used in the present study has been confirmed through FTIR analysis.

1. Introduction

The possible application of solid polymer electrolytes (SPEs) in a diversity of electrochemical appliances rises from their advantages such as high energy density, electrochemical stability and easy handling. Solid polymer electrolytes are more suitable because they have improved shape, easy to handle, and possibilities for electrolytes leaking are none [1].

Poly(vinyl alcohol) (PVA) has excellent film forming nature, high tensile strength and flexibility. It is a crystalline, synthetic water- soluble polymer and has very important application due to the role of hydroxyl groups and hydrogen bands assist in the formation of polymer blends. It has some technological advantages in electrochemical devices, fuel cells, etc [2]. All these appealing characteristics made us choose PVA.

Most of the polymer electrolytes developed by researchers are of lithium based on. But the lithium salts have some negative factors, i.e they are i) scarcely available, ii) not safety, iii) high cost. To alleviate these issues, it is needed to choose the alternate to lithium salts. Keeping this in mind, many reporters developed the SPEs with the help of sodium [3], zinc [4], potassium [5] and magnesium [6], which act as an ionic source to the polymers. Of these above, the zinc added polymer system

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has revealed greater interest compared to others.

The devices which are based on Zinc possess higher specific and volumetric energy density. Also, this system has a comparable ionic radius of Li^{+} (68 pm) and Zn^{2+} (74 pm). Therefore, we may use zinc as an insertion compound instead of lithium ions. Literature study reveals that the polymer electrolyte system based on zinc are very less. Hence, it has been decided to prepare zinc based polymer electrolyte system. For the present work, we have chosen a very simple electrolyte, zinc chloride as it is very cheap, easily available and can handle easily in atmosphere.

The present work deals with the preparation and characterization of polymer electrolytes based on PVA with $ZnCl_2$ by solution casting technique using distilled water as solvent.

2. Materials and Methods

Polymer films, PVA:$ZnCl_2$ of different compositions have been prepared using solution casting technique. First PVA is dissolved in distilled water and it was stirred well. After complete dissolution of PVA different concentrations of $ZnCl_2$ is added in the same solution and this mixture was stirred well until a homogenous solution was obtained. Then, the homogenous solution has been poured in the propylene petri dishes and allowed to evaporate in hot air oven at 60°C. From this experiment we attained a stable free standing films.

3. Characterization Techniques

3.1 AC impedance Analysis

Impedance values of the SPEs were determined with the help of Hioki impedance analyzer in the frequency range of 1 Hz – 5 MHz with a signal amplitude of 2mV using stainless steel blocking electrodes.

3.2 FTIR Analysis

The FTIR spectra were recorded using SHIMADZU FTIR spectrophotometer in the wave number region 4000 – 400 cm^{-1}.

4. Results and Discussion

4.1 AC Impedance Analysis

AC impedance plot of PVA & $ZnCl_2$ system is given in Figure 1. It contains of two clear regions, a depressed semicircle in the high frequency region and a slanted spike in the low frequency region. The semicircular portion correlates to the parallel combination of bulk resistance and capacitance. Further the semicircle which is semicircle in nature divulges the non-Debye nature of the sample owing to the potential well for each site, through which transportation of ion takes place [7].

The presence of slanted spike at low frequency region is at angle less than 90°. This is due to the roughness of the electrode-electrolyte interface.

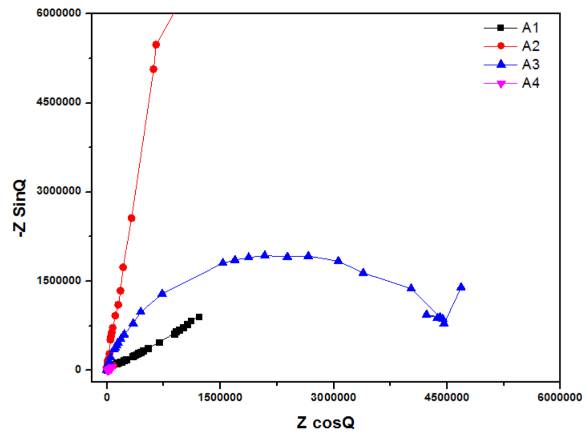

Figure 1. AC impedance plot of PVA - $ZnCl_2$ system

The intercept of the low-frequency spike at the real axis of the complex impedance plot gives the value of R_b.

The ionic conductivity (σ) of $BaTiO_3$ added polymer electrolyte system is calculated with the help of following equation

$$\sigma = \frac{l}{R_b A} \quad (1)$$

where, l represents the thickness of the prepared films, is the area of the SS electrode and is the bulk resistance.

The calculated values of ionic conductivity for PVA-$ZnCl_2$ system using Wquation (1) are given in Table 1. It is observed from the Table 1, that the value of ionic conductivity (σ) decreases against the increase of the concentration of $ZnCl_2$ from 10wt% to 30wt% in steps of 10wt%. The lesser value of ionic conductivity for 10, 20 and 30 wt% $ZnCl_2$ added system may be related to the re-association of the ions which leads to the formation of ion cluster of $ZnCl_2$ in the PVA matrix [2].

Table 1. Values of ionic conductivity PVA-$ZnCl_2$ system

Sample	PVA : ZnCl2 (wt%)	Ionic conductivity (Scm-1)
A1	90:10	2.5037×10^{-8}
A2	80:20	1.0079×10^{-9}
A3	70:30	1.0890×10^{-9}
A4	60:40	3.9194×10^{-7}

When the concentration of $ZnCl_2$ increased from 30wt% to 40%, an increase in the ionic conductivity is observed. At 40wt%, the ionic conductivity reaches a maximum value of 3.9194 x 10^{-7} Scm^{-1} which is greater by two orders of magnitude when compared with the value 2.5037 x 10^{-8} Scm^{-1} of PVA-$ZnCl_2$ (90:10) system at room temperature. This enhancement in ionic conductivity can be related to the increase in the number of mobile charge carriers [8]. The film was fragile in nature when the concentration of $ZnCl_2$ was beyond 40%. Hence, the maximum ionic conductivity of 3.9194 x 10^{-7} Scm^{-1} is obtained for PVA-$ZnCl_2$ (60:40) system.

4.2 FTIR Analysis

The FTIR spectra of pure PVA, $ZnCl_2$ salt and PVA complexed with $ZnCl_2$ salt are shown in Figure 2. The following spectral changes are observed on comparing the spectra of complexed polymer electrolyte films with those of pure PVA and $ZnCl_2$ salt.

The pure PVA has a broad peak in the range 3757–3078 cm^{-1} pertains to O-H stretching [9]. The wideness of the peak is accredited to the intra and/or intermolecular hydrogen bonding [10], and the same is found to be present for $ZnCl_2$ added PVA systems. C-H stretching of CH_2 showed a peak 2924 cm^{-1} for pure PVA [10] and is slightly shifted to 2916 cm^{-1} in 20% and 30% weight percentage of $ZnCl_2$ added systems respectively, whereas there is no shift for another weight percentage systems.

The characteristic vibrational band at 1257 cm^{-1} corresponds to C=O stretching of secondary alcohols [10] and is shifted to 1242 cm^{-1} in the complexed polymer electrolyte film. C = C stretching occurring at 1111cm^{-1} in pure PVA is shifted to 1121cm^{-1} for $ZnCl_2$ added systems. All these changes in the FTIR spectra confirm the complexation between PVA and $ZnCl_2$.

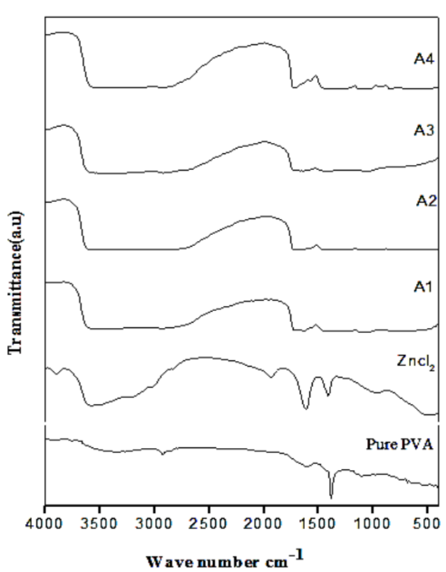

Figure 2. FTIR spectra of PVA with $ZnCl_2$ system

5. Conclusions

In this work, the structural and electrical properties of the solid polymer electrolytes based PVA and $ZnCl_2$ via solution casting technique have been studied. Maximum ionic conductivity of 3.91949 x 10^{-7} Scm^{-1} was observed for (60:40) PVA:$ZnCl_2$ system at room temperature. FTIR analysis reveals the possible bonding present in the polymer - salt complex and confirms the complex formation between the polymer and the salt.

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