

Impedance spectroscopy and structural analysis of VO₂⁺ doped Poly vinyl chloride (PVC) electrolytes

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ABSTRACT

This paper reports on structural, morphological and electrical properties of solid polymer electrolyte films based on PVC complexed with different concentrations of VO^{2+} using solution cast technique. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and impedance spectroscopy studies. X-ray diffraction (XRD) results revealed that the amorphous nature of PVC polymer matrix increased with the increase of VO^{2+} ions concentration. The electrical conductivity was evaluated from impedance spectroscopy studies in the temperature range 303- 373 K and the conductivity was found to increase with increasing dopant concentration. The polymer complexes exhibited Arrhenius type dependence of conductivity with temperature. The variation in film morphology was examined by scanning electron microscopy (SEM).

Introduction:

Solid polymer electrolytes (SPE) has attracted considerable attention in terms of its scientific importance and application in energy storage or conversion devices such as batteries, fuel cells, super capacitors etc., arising from its high ionic conductivity, electrochemical stability and good mechanical properties [1-2]. Apart from lithium salt complexes, some other electrolytes were also reported containing salts of sodium, magnesium and zinc metals [3-5]. Presently the world wide attention has focused on the high performance and environment friendly nature of energy storage devices. Lithium ion conducting polymer electrolytes are incorporated in most of the commercially available batteries for their fabrication due to its high capacity and excellent chemical stability. At the same time, lithium ion batteries are relatively expensive and suffer from safety limitations because of its explosive nature. Polyvinyl chloride (PVC) is one of the most important commercial polymers that has wide range of applications. PVC is a linear, thermoplastic, substantially amorphous polymer, with a huge commercial interest due to the accessibility to basic raw materials and to its properties. It is used as thermoplastic due to its many valuable properties like low price, good process ability, chemical resistance, good mechanical strength, thermal stability and low flammability. Currently, PVC is one of the world's leading synthetic polymers with global consumption of approximately 40 million tonnes per annum [6, 7].

Among the transition metal ions, VO^{2+} ion has been extensively used as a probe to study the symmetry of the crystalline electric field. Vanadium oxides have also shown promise as optical switching materials on the basis of their electro-chromic properties [8-11]. The properties of the VO^{2+} doped PVC polymer films have been reported in this paper.

Experimental

Poly vinyl chloride (PVC) obtained from M/S Sigma Aldrich has a mean relative molecular mass of about 534,000 g/mol. PVC polymer films doped with $VOSO_4$ in various concentrations were prepared at room temperature by solution casting method. The desired concentration of $VOSO_4$ solutions (1, 2, 3, 4 and 5%) were prepared by using distilled water. 1g/mol of PVC polymer is dissolved in tetra hydro furan (THF) separately. Different amounts of $VOSO_4$ solution (1, 2, 3, 4 and 5 mol%) were added into the polymer solution. The mixture was magnetically stirred for 10-12 hours to get homogeneous mixture and then cast onto glass dishes. The film was slowly evaporated at room temperature to obtain free standing polymer film at the bottom of the dishes.

In order to investigate the nature of the polymer electrolytes, the electrical properties of the polymer electrolyte films were measured by a computer controlled impedance analyzer (Agilent E4980 precision LCR meter, USA) over the frequency range 20 Hz - 2 MHz with a signal level of 10 mV. The measurements were carried out by sandwiching the polymer electrolyte film between two stainless steel electrodes in the temperature range of 303 – 373 K. X-ray diffraction measurements were carried out using a BRUKER D8 ADVANCE diffractometer with $CuK\alpha$ radiation (1.5406 Å). The films were

scanned at 2θ angles between 10° and 80° with a step size of 0.02° . The morphology of the polymer films was characterized by the JEOL JSM 840A electron microscope (SEM) with scanning attachment.

Results & Discussion:

Impedance analysis:

In solid state ionic batteries, the polymer electrolytes work as a separator as well as medium to transport ions from anode to cathode. Hence, ionic conductivity of polymer electrolyte is a very important parameter for battery applications. Figure 1 shows the impedance spectra of PVC doped with different concentrations of VO^{2+} based polymer electrolytes at room temperature. Typical AC impedance plot shows two well – defined regions: (1) depressed semi-circle at high frequency side and (2) inclined line at low frequency side. In PVC: VO^{2+} , the depressed semicircle, observed in the high-frequency region at 2 – 5 mol% of VO^{2+} is due to the bulk effect of the electrolytes and the linear region in the low-frequency range is attributed to the effect of the blocking electrodes [12]. The disappearance of high frequency semicircular portion leads to a conclusion that the current carriers are ions and hence the total conductivity is mainly the result of ion conduction. The bulk resistance (R_b) can be retrieved from the intercept of high frequency semi-circle or the low frequency spike on the Z' - axis [13]. The ionic conductivity values of the electrolytes are calculated by using the equation:

$$\sigma = \frac{d}{R_b A}$$

Where, d and A are the thickness and known area of the electrolyte film respectively and R_b is the bulk resistance of the electrolyte film. From the figure, it is seen that the conductivity of pure PVC is about $4.87 \times 10^{-8} \text{ Scm}^{-1}$ at room temperature and the highest conductivity has been found to be $2.68 \times 10^{-6} \text{ Scm}^{-1}$ at room temperature for PVC-5 mol% VO^{2+} polymer electrolyte. The increase in ionic conductivity with the addition of VO^{2+} is attributed to a reduction in crystallinity of copolymer electrolyte and also the increase in number of mobile charge carriers. The coordination interactions of the ether oxygen atoms of PVC with VO^{2+} cations, which result in a reduction in crystallinity of PVC copolymer, are responsible for the increase in ionic conductivity.

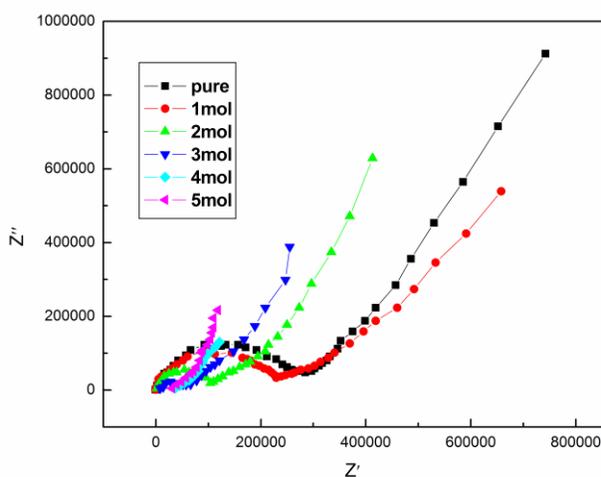


Figure 1: Room-temperature Nyquist impedance plots of VO^{2+} ions doped PVC polymer electrolyte films.

Concentration dependence of conductivity:

The conductivity at room temperature of the pure PVC is found to be $4.87 \times 10^{-8} \text{ Scm}^{-1}$. This study shows that the addition of VO^{2+} ions increases the ionic conductivity of PVC. Figure 2 shows that the variation of ionic conductivity of PVC: VO^{2+} polymer electrolyte system with different concentration of VO^{2+} ions. The spectra show that the conductivity increases with an increase in concentration. The initial increase in conductivity is due to the availability of free mobile ions [14].

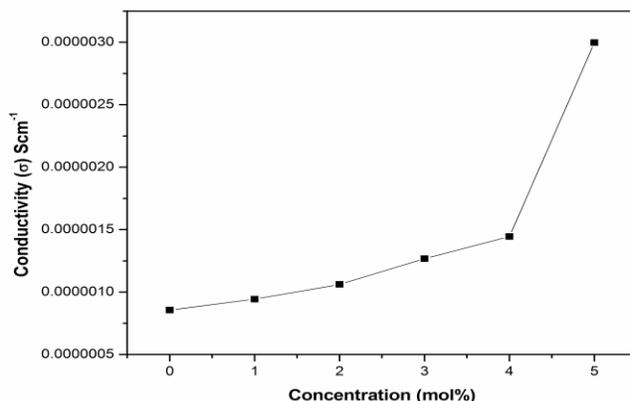


Figure 2: Room-temperature ionic conductivity as a function of VO^{2+} concentration for the PVC polymer electrolyte system.

Temperature dependence conductivity:

The solid polymer electrolytes follow Arrhenius as well as Vogel-Tamman-Fulcher (VTF) types of ionic conduction which depends on the type of the salt, polymer and the temperature range [15]. Figure 3 represent the temperature dependence of ionic conductivity for all compositions of PVC: VO^{2+} systems. From the plot it has been observed that as temperature increases the conductivity values also increases for all the compositions. The experimental data indicate that the ionic conductivity is enhanced with increasing temperature at high salt concentration. When the temperature is increased, the mobility of polymer chain is enhanced, and the fraction of free volume in the polymer electrolyte system increases accordingly, which facilitates the transitional motion of ions [16]. Thus the segmental motion either allows the ions to hop from one site to other site, or it provides pathway for ions to move, which leads to an increase in ionic conductivity of the polymer electrolyte.

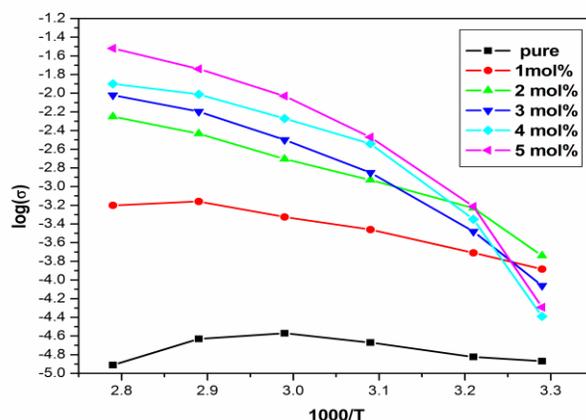


Figure 3: Nyquist impedance plots of the polymer electrolyte film with VO^{2+} at different temperatures.

X-ray diffraction studies

XRD analysis is very useful in determining the structure of the polymer electrolytes. Figure 4 represents the X-ray diffraction of pure and doped PVC polymer electrolytes with different concentrations of VO^{2+} . For pure PVC a broad peak was observed at 2θ region of $11\text{--}18^\circ$ which can be attributed to the amorphous nature of pure PVC. This peak is broadened and its relative intensity decreases with increase of VO^{2+} concentration, which indicates the increase in the amorphous nature of the host polymer. The increase in the amorphous nature causes a reduction in the energy barrier to the segmental motion of the polymer electrolyte. This amorphous nature results in greater ionic diffusivity and high ionic conductivity, which can be observed in amorphous polymers having flexible back-bone [17, 18].

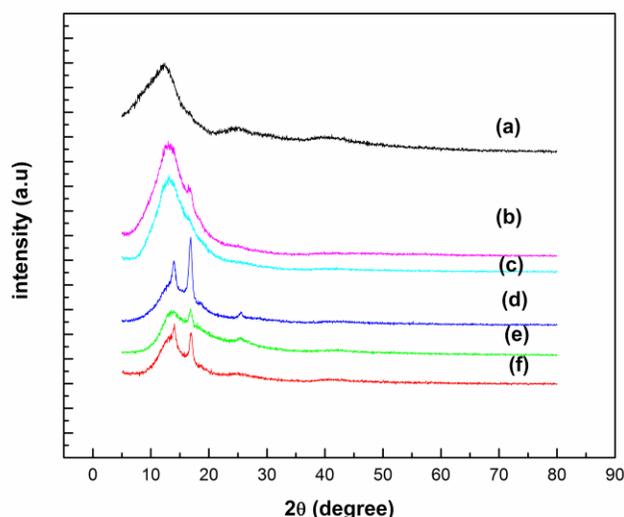


Figure 4: XRD patterns of PVC polymer films containing VO^{2+} (a) pure (b) 1mol% (c) 2mol% (d) 3 mol% (e) 4 mol% (f) 5 mol%

Scanning electron microscopy analysis

SEM images of pure and VO^{2+} doped polymer electrolytes are shown in Figure 5(a-f) respectively. Small craters are observed on the SEM images, formed due to evaporation of the solvent during preparation of the thin film [19]. It can be observed by comparing Figure 5(a-f) that the pore size of 5 mol% of VO^{2+} doped PVC is much smaller and its pore surface distribution is better than that of other polymer electrolytes. Compared to the other polymer electrolytes, 5 mol% of VO^{2+} doped PVC has the highest ionic conductivity and shows less phase separation, more homogeneity, indicating that the polymer and salt are completely dissolved. It can be inferred that when the molar ratio of dopant concentration is high in the polymer matrix an agglomeration of dopant takes place. Therefore, phase separation takes place in this polymer electrolyte system. As a result, the charge carriers are transported very slowly in the presence of blocking phase leading to decrease in ionic conductivity [20, 21] in 1 to 4 mol% of VO^{2+} doped PVC films.

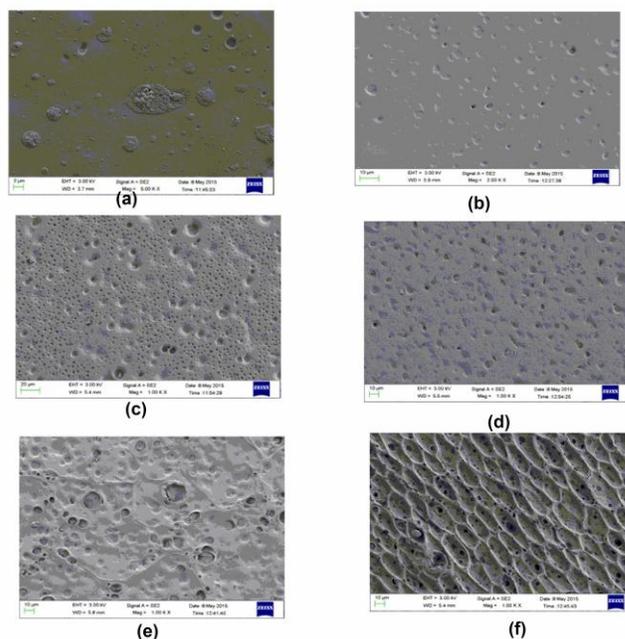


Figure 5: SEM photographs of pure and VO^{2+} doped PVC polymer films (a) pure (b) 1mol% (c) 2 mol% (d) 3 mol% (e) 4 mol% (f) 5 mol%

Conclusion:

In summary, Solid polymer electrolytes based on poly (vinyl chloride) (PVC) doped with VO^{2+} at different concentration were prepared using solution cast technique and it could be concluded that the structural, morphological and electrical properties of PVC polymer electrolyte films can be influenced by complexing it with VO^{2+} . X- ray diffraction (XRD) results revealed that the amorphous nature of PVC polymer matrix increased with the increase of VO^{2+} ions concentration. Electrical conductivity was measured with an AC impedance analyzer in the frequency and temperature range 1 Hz-1 MHz and 303 K-373 K respectively. The conductivity of pure PVC is about $4.87 \times 10^{-8} \text{ Scm}^{-1}$ at room temperature and the highest conductivity has been found to be $2.68 \times 10^{-6} \text{ Scm}^{-1}$ at room temperature for PVC-5 mol% VO^{2+} polymer electrolyte. The increase in ionic conductivity with the addition of VO^{2+} is attributed to a reduction in crystallinity of copolymer electrolyte and also the increase in number of mobile charge carriers.

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