

Synthesis and Study of PVA Based Gel Electrolyte

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Abstract: An attempt has been made to prepare polyvinyl alcohol (PVA) based proton conducting gel electrolytes in ammonium thiocyanate (NH_4SCN) solution and to characterize them. XRD studies revealed that the entire gel sample are amorphous in nature with a broad peak at nearly $2\theta=22^\circ$. Variation of conductivity of gel electrolyte with loading concentration of PVA has also been studied. It has been observed, as loading of PVA in 0.2 M electrolyte of $\text{NH}_4\text{SCN}+\text{DMSO}$ increases conductivity decreases. The conductivity of gel electrolytes exhibits liquid like nature at low polymer concentration while the behaviour is seen to be affected by the formation of PVA- NH_4SCN complexes upon increase in polymer content beyond 2 g. Temperature dependence of ionic conductivity exhibits VTF and Arrhenius behaviour.

Keyword: PVA, Gel electrolyte, $\text{NH}_4\text{SCN}+\text{DMSO}$, X-RD, Ionic conductivity

Introduction

During the last decades, there was a lot of effort done on the electrochemical preparation of polymer gel electrolytes. Polymer electrolytes have become material of great importance for use in different electrochemical devices due to their unique characteristics such as easy mouldability, good electrode -electrolyte contact and light weight^{1,2}. These polymer electrolytes form a bridge between liquid electrolyte and polymer. Because of their high ionic conductivity, gel electrolytes have attained precedence over conventional polymer electrolyte. In recent years, polymers such as polyvinyl alcohol (PVA), poly(vinylidene fluoride) (PVdF), polyethylene glycol (PEG), poly(vinylchloride) (PVC), poly(acrylonitrile) (PAN), poly(vinylpyrrolidone)(PVP) and poly(vinyl sulfone) (PVS) have been prominently used in development of gel polymer electrolytes^{1,3-5}. These electrolytes have been found to possess ionic conductivity, electrochemical stability and transport properties similar to their liquid counterpart along with better dynamical properties suitable for electrochemical applications. Among the listed polymeric hosts, polyvinyl alcohol have been intensely investigated, because of its interesting properties and applications. PVA is a prominent polymer because of its good solvent holding capability and wide temperature window^{6,7}. Awadhia *et al.*⁸ have reported PVA based proton conducting gel electrolyte with high ionic

conductivity. Moreover, because of the nontoxic nature of PVA, they are particularly suitable for biomedical application like artificial tissue. Thus, in the present investigation, an attempt has been made to synthesize and characterization of PVA based gel electrolytes with ammonium salt for proton conduction.

Experimental

In the present investigation polyvinyl alcohol, ammonium thiocyanate (NH_4SCN) and aprotic solvent dimethyl sulfoxide (DMSO) AR grade, s.d fine chem. Make were used for synthesis of proton conducting gel without any further purification.

Synthesis

For the synthesis of PVA gel, 30 mL electrolyte of 0.2 M solution of NH_4SCN +DMSO was prepared. PVA was added in the electrolyte at 70°C with constant stirring and continued for one hour maintaining the temperature. Then it was allowed to cool to room temperature so as to form the gel. PVA has been added in the electrolyte in different amount 0.5, 1, 1.5, 2 and 2.5 by weight (in g) to form the gel of various concentration of PVA.

Measurement technique

Structural morphology of PVA gel electrolytes have been carried out by x-ray diffractometer. The gel electrolytes were sandwiched between two platinum electrodes and conductivity measurements were performed on 304 Systronic Conductivity Bridge at various temperatures ranging from 273 K to 373 K.

Results and Discussion

XRD analysis

Figure 1 -depicts the XRD pattern for three different concentrations of PVA gel electrolytes. As seen from the Figure 1 a broad peak is noticed for the 2 g and 2.5 g PVA gel electrolytes at $2\theta=22^\circ$, the slight shift of the peak is observed in 1.5 g PVA gel electrolyte. The broadening of XRD peaks with increasing concentration indicate enhancement in the amorphous nature of gel electrolyte⁹. Thus our results are in good agreement with authors^{10,11}.

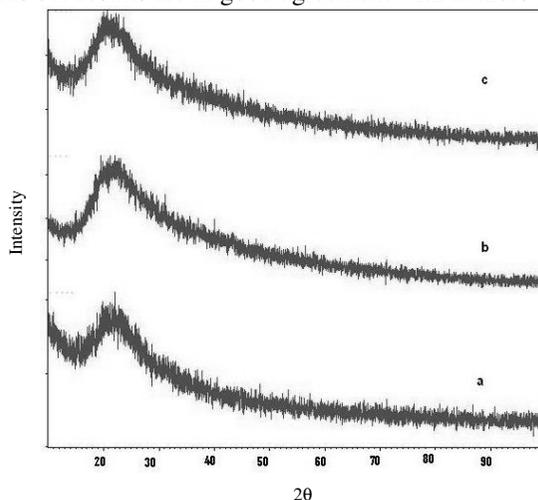


Figure 1. X-ray diffractogram of (a) 1.5 g, (b) 2 g and (c) 2.5 g PVA gel electrolytes

Conductivity studies

Figure 2 depicts the variation of conductivity ($\log \sigma$) with various concentration of PVA (in g) in liquid electrolyte at room temperature. It is observed that, conductivity decreases as concentration of PVA increases. This can be explained as follows

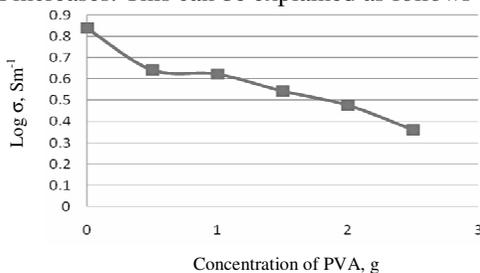


Figure 2. Variation of conductivity as a function of polymer concentration

Dimethyl sulfoxide is a highly aprotic solvent and ammonium thiocyanate is likely to dissociate into respective ions and behaves as liquid electrolyte as reflected from high conductivity value. When polymer was added to this liquid electrolyte to form gel, the conductivity was initially seen to drop down significantly. The ionic conductivity is generally dependent upon both the charge carrier concentration (n) and carrier mobility (μ). As described by relation¹².

$$\sigma = nq\mu$$

With q representing the charge of mobile carrier. Here charge carrier concentration (n), depends upon the dissociation energy (U), involved and dielectric constant (ϵ) as

$$n = n_0 \exp(-U / \epsilon kT)$$

Where, k is the Boltzmann constant and T the absolute temperature. Addition of PVA in electrolyte like NH_4SCN enhances the viscosity of the system which causes a fall in mobility of charge carrier causes a significant fall in ionic conductivity of gel electrolyte. Our results are in good agreement with authors^{12,13}.

Temperature dependence conductivity

Figure 3 shows the temperature dependence of conductivity of 0.2 M NH_4SCN electrolyte along with PVA gel electrolytes. From Figure 3 it is observed that for liquid electrolyte and all the samples of PVA gel electrolytes as temperature increases conductivity increases.

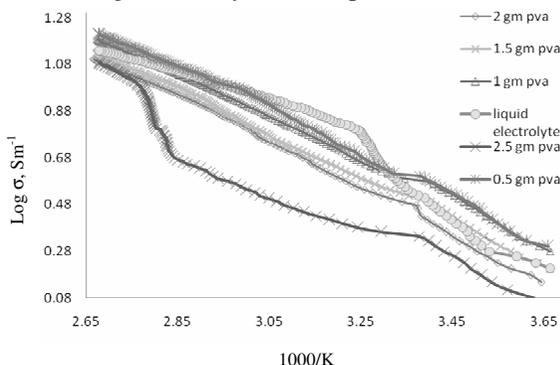


Figure 3. Conductivity as a function of temperature for liquid gel electrolyte

The conductivity of liquid electrolyte changes with temperature this might be because of dissociation in liquid is a consequence of increasing the concentration of mobile ion with temperature is unlikely¹³. The PVA gel electrolytes appear to follow a behavior similar to that of liquid electrolyte particularly at lower concentration of PVA. Though the variation of conductivity with temperature for liquid electrolyte is different from that of gel electrolyte, the rate of increase in conductivity with temperature in two cases is gradual and within an order of magnitude. The conductivity of liquid electrolyte is higher than gel electrolytes. All the curves display similar behavior *i.e.* combination of Arrhenius and VTF behavior. Arrhenius region is noted in low temperature region, while VTF nature is exhibited at higher temperature¹⁴. The low temperature Arrhenius behavior is on the account of the presence of liquid electrolyte encapsulated by the PVA matrix. As temperature raised beyond 307 K segmental motion of polymer in polymer gel electrolyte comes into play and start affecting the conductivity, leading to VTF nature described by following relation¹⁰.

$$\sigma = \sigma_0 \exp(-B/T - T_0)$$

Where, σ_0 is the pre exponential factor, B is constant related to activation energy and T_0 is reference temperature associated with ideal Tg. The change in nature of gel electrolyte in the temperature region 289 K to 307 K is due to transition of polymorphic phase in polyvinyl alcohol. Such features are generally observed for highly amorphous polymeric system. Since the experimental PVA gel samples are found to be highly amorphous as confirmed from XRD study. The increase in conductivity with temperature is interpreted as hopping mechanism between coordinated sites, local structural relaxation and segmental motion of the polymer. As the amorphous region progressively increases, however, the polymer chain acquires faster internal motion and bond rotations. This in turn favors the hopping of inter-chain and intra-chain movement and ionic conductivity of polymer electrolyte becomes high.

Besides exhibiting VTF behavior the temperature dependence of conductivity also depicts significant variation for the gel electrolyte containing higher amount of PVA *i.e.* beyond 2 g of PVA, on account of formation of PVA – NH₄SCN complex. Our results are in good agreement with Shukla *et al.*⁷, Patel¹⁰, Sekhon *et al.*¹⁵, Chand *et al.*¹⁶ and Pandey *et al.*¹⁷.

Conclusion

Polymer gel electrolytes prepared by addition of PVA in 0.2 M NH₄SCN in DMSO have been structurally and electrically characterized in the present work. XRD patterns exhibit broadening of peak in diffraction patterns for 2.5 g PVA gel electrolyte indicating increase in amorphousness. Gel of higher concentration of PVA shows the presence of PVA: NH₄SCN complex and conductivity is seen to be influenced by the presence of this complex. Temperature dependence of ionic conductivity of gel electrolyte reflects Arrhenius and VTF behaviour.

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