

Morphology, thermal, electrical and electrochemical stability of nano aluminium-oxide-filled polyvinyl alcohol composite gel electrolyte

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Abstract. In the present work, an attempt has been made to develop nano aluminium oxide (Al_2O_3)-filled polyvinyl alcohol (PVA) composite gel electrolytes. Surface morphological studies, thermal behaviour, electrochemical stability and electrical characterization of these composite gel electrolytes have been performed. An increase in the concentration of Al_2O_3 in composite gel electrolytes increases the amorphous characteristics of pure PVA. Bulk conductivity of composite gel electrolytes increases by an order of magnitude on addition of a nano filler. Maximum conductivity of 5.81×10^{-2} S/cm is observed for 6 wt% Al_2O_3 -filled polymer gel composite electrolytes. Temperature dependence of electrical conductivity shows a combination of Arrhenius and Vogel–Tamman–Fulcher (VTF) nature. Maximum current stability during oxidation and reduction cycle is noticed for 6 wt% Al_2O_3 -filled PVA composite electrolyte, viz. ± 1.65 V.

Keywords. Polymer nanocomposite gel electrolytes; ionic conductivity; polymer electrolytes; X-ray diffraction; differential scanning calorimetry.

1. Introduction

Polymer electrolytes have become materials 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 (MacCallum and Vincent 1989; Gray 1991). These polymer electrolytes form a bridge between liquid electrolyte and solvent-free ceramics (Scrosati and Vincent 2000). Because of their high ionic conductivity, gel electrolytes have attained precedence over conventional polymer electrolytes. In recent years, polymethylmethacrylate (PMMA) (Bohnke *et al* 1992; Sekhon 2003; Singh *et al* 2005), polyacrylonitrile (PAN) (Croce *et al* 1994), polyvinylidene fluoride (PVdF) (Song *et al* 2000; Sekhon 2003) and polyethylene oxide (PEO) (Radhucha *et al* 1996; Sekhon 2003) have been reported as suitable polymer host material for the preparation of polymer gel electrolytes.

Literature survey has revealed that most of the work reported on polymer gel electrolytes concerns development of lithium-based polymer batteries (Koksbang *et al* 1994; Caravanier *et al* 2003; Sekhon 2003; Sato *et al* 2005). Proton conductors are equally important class of electrolyte materials due to their applications in fuel cells, electrochromic devices (ECDs) and other smart devices

(Colomban 1992). Within the family of proton conductors, work on PEO-based gel electrolytes with strong acids like H_3PO_4 , H_2SO_4 and HCl (Wieczorek *et al* 1995; Radhucha *et al* 1996), and PMMA-based gel electrolytes containing benzoic and dicarboxylic acids (Chandra *et al* 2000; Song *et al* 2000; Sekhon *et al* 2002; Sekhon 2003) have been reported in recent years. Within the umbrella of polymer gel electrolytes, PVA is also one of the prominent polymers because of its good solvent holding capability and wide temperature window (Finch 1973). Moreover, it is known to form a good gel material for medical applications (Cavaliere *et al* 2003). Awadhia and Agrawal (2007) have reported PVA-based proton-conducting gel electrolyte with high ionic conductivity. However, when most of the studied gel electrolytes are retained for a long period, exudation of liquid from gel lump occurs, which causes instability in device performance. As synthesized gel electrolytes of polyvinyl alcohol: dimethyl sulphoxide: ammonium thiocyanate (PVA: DMSO: NH_4SCN) also show similar behaviour with aging (Awadhia and Agrawal 2007), which limits its utility in practical devices when operated over long periods. Therefore, with anticipation of better stability under ambient conditions such as-synthesized gel electrolytes are usually doped with inorganic/organic fillers leading to the formation of composite gel electrolytes (Honma *et al* 1999; Ray and Okomota 2003; Koo 2006; Agrawal and Pandey 2008; Duangkaew and Woothikanokkhan 2008). A similar approach has been tried in the present work to

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improve the performance of PVA:DMSO:NH₄SCN electrolytes by dispersal of nano-sized Al₂O₃ filler particles. This system is expected to drastically impede crystallization process in polymer-based nanocomposite electrolytes and thus improve ionic conductivity, mechanical integrity as well as its electrochemical stability for long-term use in electrochemical devices, particularly smart windows, owing to the possibility of single ion conduction (Agrawal and Shukla 2000). Freestanding films were prepared by conventional solution cast technique and subsequently characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), cyclic voltammetry (CV) and conductivity measurements.

2. Experimental

In the present investigation, PVA (average molecular weight 124,000–186,000; Aldrich make), ammonium thiocyanate (NH₄SCN), AR grade (s.d. fine chem make) and aprotic solvent dimethyl sulphoxide (DMSO) (Merk Limited, Mumbai) were used for synthesis of composite gels. Al₂O₃ used in the study was obtained from Alfa Aesar, CAS Number: 1344-28-1 and the size of the particles was between 40 and 50 nm. PVA was dispersed in 1 M salt solution of NH₄SCN in DMSO in different stoichiometric ratios to form pristine gel electrolyte (PVA:NH₄SCN system). Composite polymer gel electrolytes were prepared by adding Al₂O₃ nanoparticles in pristine gel electrolyte solution in different weight proportions followed by thorough mixing at slightly elevated temperature on a magnetic stirrer. The so-formed solutions were poured in PC petri dishes and covered with Al foils to avoid contamination. After syneresis, gels in the form of thick films were taken out and dried at room temperature for few a days to obtain stable gel electrolytes. The resulting gel films were stored carefully to avoid exudation of solvent. Structural morphology of different polymer nanocomposite electrolytes were studied by X-ray diffractometer (model no. RIGAKU JAPAN MINIFLEX-II). The diffraction pattern was recorded at room temperature (~25°C) for the Bragg angles (2θ) varying from 2° to 90° with the scan speed of 2 min⁻¹. SEM images of different polymer nanocomposite electrolyte system were recorded with JEOL JSM-6390A instrument. The complex-impedance measurements were carried out with help of a computer-controlled Hioki (Japan) make LCR meter (Model 3520). After sandwiching the composite gel electrolytes sample between two platinum electrodes, electrical conductivity measurements were performed in the frequency range varying from 40 Hz to 100 kHz at various temperatures ranging between 300 and 373 K. The thermal behaviour of Al₂O₃ nanoparticle-filled PVA gel electrolytes were observed using a Mettler Toledo DSC model 822e. Differential scanning calorimetry (DSC) runs were recorded at

10°C min⁻¹ heating rates for unfilled and 2, 4, 6 wt% nanoparticle (Al₂O₃)-filled PVA gel electrolytes. The DSC scans of these samples were carried out only to measure glass temperature (T_g) and melting temperature (T_m) in the temperature range 40–240°C. Cyclic voltammetry analysis was carried out in air at room temperature using an Electrochemical Analyzer (CH Instruments, USA model no. CHI608D) in the voltage sweep range ± 3 V keeping the scan rate at 0.1 V s⁻¹. Current–time measurements on the samples were conducted to estimate ionic transference number and nature of charge transport.

3. Results and discussion

3.1 Morphology studies

Figures 1a–d depicts the surface morphology of DMSO:NH₄SCN:PVA electrolyte films containing 0, 2, 6 and 10 wt% concentration of Al₂O₃ nanofiller. Unfilled PVA gel electrolyte shows a closed pore structure made up of PVA chains. Addition of 2 wt% Al₂O₃ nanoparticles reduces the porosity of PVA composite electrolyte because Al₂O₃ nano particles are entrapped between chains in the pores (figure 1b). White coloured spots observed in the SEM image show that Al₂O₃ nanofiller particles are not fully absorbed. On addition of 6 wt% Al₂O₃ nano particles (figure 1c), chains of PVA are fully covered with Al₂O₃ nanoparticles. This indicates complete dispersion of Al₂O₃ nanofiller in electrolyte film. On further addition of Al₂O₃ nanoparticles in the system, separate grains comprising of Al₂O₃ nanoparticles and PVA electrolyte are formed. Grains are of irregular size and shape, confirming its partial crystalline texture.

3.2 XRD studies

The XRD patterns of polymer gel electrolytes films of DMSO:NH₄SCN:PVA without and with Al₂O₃ nanofillers along with pristine materials are shown in figure 2a–h. These patterns show an increase in amorphousity of polymer electrolyte after addition of salt and Al₂O₃ nanofiller. The intense XRD pattern for DMSO casted PVA film (figure 2c) exhibits a moderately broad peak around 19.6°, which shifts to lower 2θ value in PVA:NH₄SCN:DMSO (figure 2d) gel electrolyte. Recently, this shifting of PVA-related peak has been correlated to complexation of pristine components leading to the formation of polymer gel electrolyte (Awadhia and Agrawal 2007). Upon addition of Al₂O₃ nanofiller, the peak broadens and shifts toward higher 2θ values. Further, no peak related to Al₂O₃ (figure 2a) could be tracked. This feature ascertains improvement in system morphology with complete absorption of Al₂O₃ particles in the PVA matrix. At higher concentrations of Al₂O₃, the characteristic reflections of Al₂O₃ nanofiller start reappearing

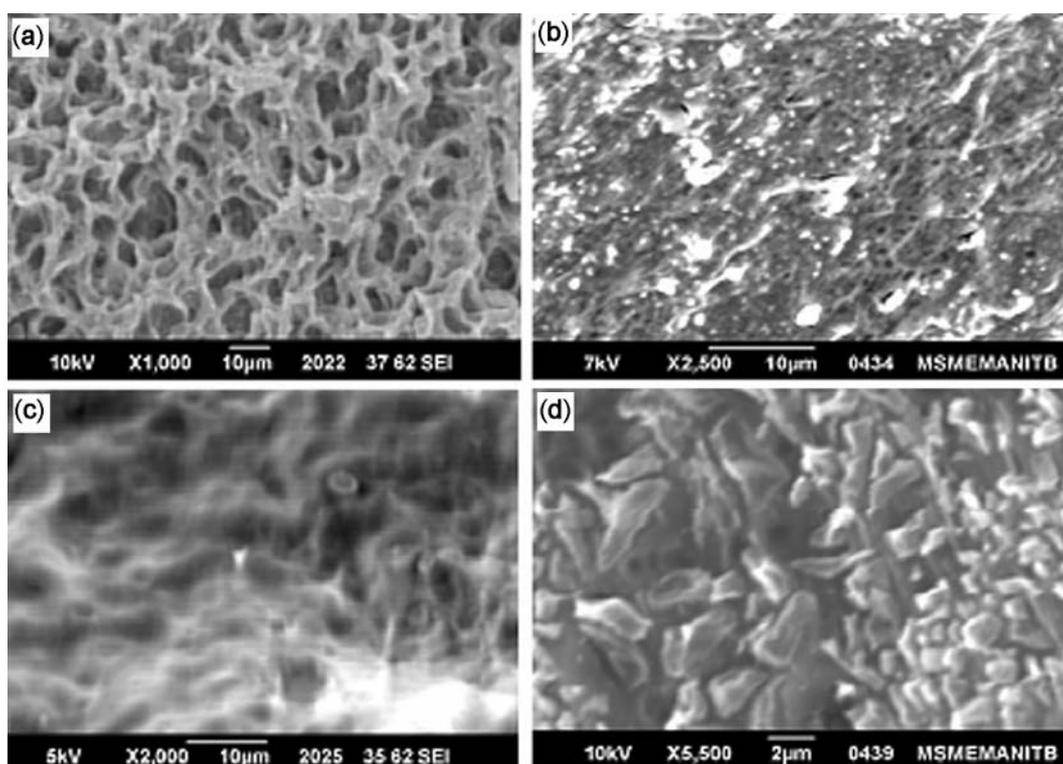


Figure 1. SEM images of (a) DMSO casted PVA : NH₄SCN gel electrolyte and its composite containing (b) 2 wt%, (c) 6 wt% and (d) 10 wt% Al₂O₃ filler.

because of its segregation. From the XRD study, it is concluded that Al₂O₃ nanofillers are homogeneously dispersed throughout the polymer matrix with maximum uptake of 6 wt%. The strong and sharp diffraction peaks in Al₂O₃ and NH₄SCN indicate high crystallinity of the obtained products, which disappears in case of polymer composites due to enhancement in amorphous nature of electrolytes. Degree of crystallinity, X_c of electrolytes with respect to Al₂O₃ was estimated to ascertain improvement in amorphous nature (Cullity 1978) presuming the filler to be fully crystalline (table 1). Likewise, the average crystallite size in composite system (table 1) was also estimated using the well-known Debye–Scherrer relation (Cullity 1978). This too shows an enhancement in amorphous behaviour of composite electrolytes up to 6 wt% Al₂O₃ concentration and thereafter it decreases, i.e. improvement in crystalline behaviour. All these results clearly indicate improvement in system morphology up to 6 wt% filler addition.

3.3 DSC studies

DSC thermograms of figure 3, represent the thermal scans for pure PVA (scan a), NH₄SCN (scan b), Al₂O₃ nanofiller (scan c) and PVA : NH₄SCN : DMSO electrolyte (scan d) along with a few nano-filled composite gel electrolytes. It is well established that both crystalline and amorphous phases coexist in most of the polymers

(Tager 1978; Bhat and Deshmukh 2002). PVA is a partially crystalline polymer which exhibits both the glass transition and melting transition. The glass transition temperature and melting temperature of PVA is seen to occur at 88 and 216°C, respectively (scan b). These transitions are in close proximity to the earlier reported values (Gong *et al* 1989; Shukla and Agrawal 2000). A broad shoulder peak around 170°C is also witnessed in the DSC profile of pure PVA. Such a feature has also been reported earlier (Zou *et al* 2008) and ascribed to phenton melting (Mukherjee *et al* 2004). DSC thermogram for pristine gel electrolyte used in the development of composite system has also been recorded (scan d). In consonance with earlier reports (Shukla and Agrawal 2000; Awadhia and Agrawal 2007), pristine electrolyte thermogram (scan d) depicts four endothermic transitions including two small shoulders related to phenton melting, PVA : NH₄SCN : DMSO complex and uncomplexed PVA, respectively. Since composite polymer gel electrolytes are characterized by salt solution (liquid electrolyte) trapped within the polymer network, the thermal behaviour of polymer composite gel electrolytes is expected to be affected by the interaction between components present in it. On adding 2 wt% of Al₂O₃ nanoparticles in pristine gel electrolyte to form composite gel electrolyte, the melting point of salt and PVA appears in the temperature range 433–513 K (scan e) in addition to the broadness in endothermic transitions (Shukla and Agrawal

Table 1. Average crystallites size, crystallinity, ionic transference number and activation energy of as-synthesized composite gel electrolyte system (PVA : DMSO : NH₄SCN : Al₂O₃).

Sl. no.	Concentration of Al ₂ O ₃ content in Pristine electrolyte (wt%) ^a	Average crystallites size (nm)	Crystallinity, X _c (%)	Ionic transference number, <i>t</i> _{ion} ^b	Activation energy, E _a (eV) ^c
1	0	~ 45	65.9	0.94	0.081
2	4	~ 38	46.3	0.96	0.058
3	6	~ 37	32.2	0.98	0.047
4	8	~ 42	44.8	0.97	0.053
5	10	~ 41	72.7	0.95	0.083

^aPristine electrolyte (prepared by adding 5 wt% PVA in 1 M NH₄SCN salt solution in DMSO).

^bIonic transference number calculated using relation (i).

^cActivation energy calculated from log σ vs 1000/T plot (figure 8) in Arrhenius region.

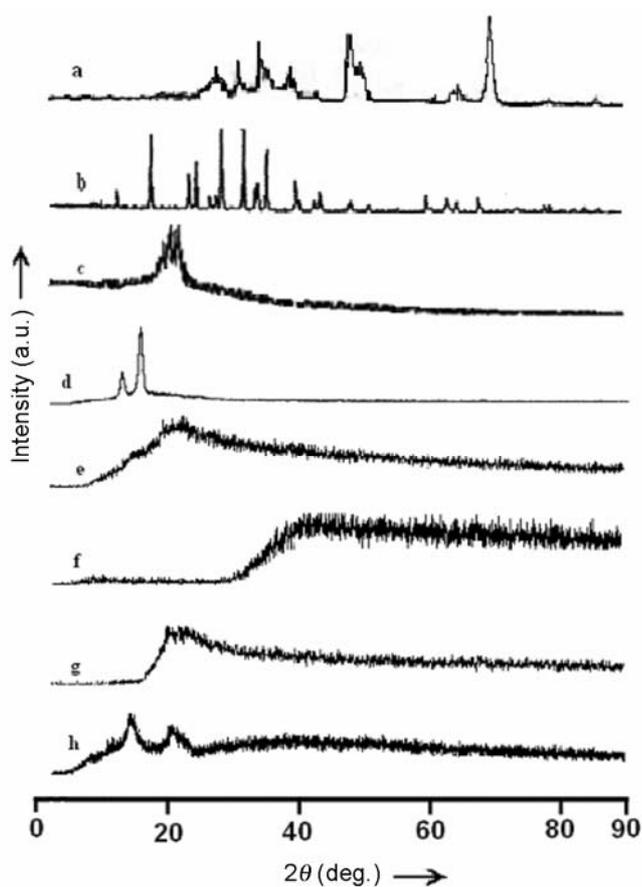


Figure 2. X-ray diffractograms of (a) Al₂O₃ nanoparticles, (b) NH₄SCN, (c) DMSO casted PVA gel film (d) DMSO casted PVA:NH₄SCN gel electrolyte and its composite containing (e) 4 wt%, (f) 6 wt%, (g) 8 wt% and (h) 10 wt% Al₂O₃ filler.

2000; Awadhia and Agrawal 2007). The observed broadness results from coexistence of uncomplexed salt (NH₄SCN), PVA : NH₄SCN complex, excess DMSO and uncomplexed PVA-related endothermic transitions. The presence of partially complexed component PVA : NH₄SCN is also visible in the DSC thermogram of gel films containing higher filler content (4 wt% and 6 wt% Al₂O₃ nanoparticle, viz. scans f and g). DSC thermograms

further indicate a strong endothermic transition around 430 K which shifts to higher temperature on addition of nanofiller up to 4 wt%. Such a shift may be due to encapsulation of system and attachment of methyl group of DMSO with polar group of PVA, leading to gelification. The retrieval of this transition at 6 wt% can be attributed to agglomeration of nanoparticles as also seen in XRD and SEM analysis.

3.4 Wagner's polarization

Figure 4 depicts the Wagner's polarization curves for two composite gel electrolyte samples. The ionic transference number *t*_{ion} was evaluated using the following relation:

$$t_{\text{ion}} = \frac{I_{\text{initial}} - I_{\text{final}}}{I_{\text{initial}}} = \frac{I_{\text{total}} - I_{\text{electronic}}}{I_{\text{total}}} = \frac{I_{\text{ionic}}}{I_{\text{total}}}, \quad (1)$$

where *I*_{ionic} is the current due to ions, *I*_{electronic} (or *I*_{final}) the current due to electrons, and *I*_{total} (or *I*_{initial}) the sum of ionic and electronic contribution to current.

It is observed that the nature of charge transport is similar to that for solvent-free gel polymeric electrolytes (Shukla and Agrawal 2000). Moreover, the charge transport appears to exist when mobile ions are trapped within the polymer–matrix complex. It is noticed from table 1 that *t*_{ion} gradually increases (up to 0.98) upon addition of Al₂O₃ nanoparticles up to 6 wt% and thereafter it decreases. Such a behaviour can be associated to loss of ionic conductivity after adding more than 6 wt% of Al₂O₃ nanoparticles in PVA gel electrolytes.

3.5 Conductivity studies

Figure 5 shows the effect of salt concentration on ionic conductivity of Al₂O₃ nanoparticles-filled PVA : NH₄SCN : DMSO polymer gel electrolytes. Conductivity of composite gel electrolyte samples has been extracted with the help of Z' versus Z'' data. Agrawal and Awadhia (2004) have recently reported the effect of salt variation on ionic conductivity of DMSO : NH₄SCN : PVA gel

electrolytes. It has been shown that complex formation takes place in the system, which tends to raise the conductivity of the system through greater dissociation of salts. Upon dispersal of 4 wt% Al_2O_3 nanoparticles in pristine gel electrolyte to form nanocomposite gel electrolyte, the bulk conductivity is seen to rise with salt molarity and attain an optimum at 1 M salt concentration. This conductivity behaviour corresponds to that for liquid electrolyte although the magnitude is lower for optimum conductivity (Patel *et al* 2007). This correspondence of conductivity response reflects the presence of trapped liquid electrolyte within polymer matrix, which affects the conductivity of composite system. It has been shown earlier in morphological studies (figure 1) that upon addition of Al_2O_3 nanoparticles in pristine electrolytes, they get entrapped within the chains in the pores. This affects the solvent holding capacity of matrix electrolyte and hence the conductivity. Thus, when the polymer and nano-

filler components are present in a composite gel system, the polymer matrix not only works as stiffener but also affects ionic conduction. At lower concentrations of salt, full dissociations of salt into respective ions may be considered and there is nothing to be dissociated by the

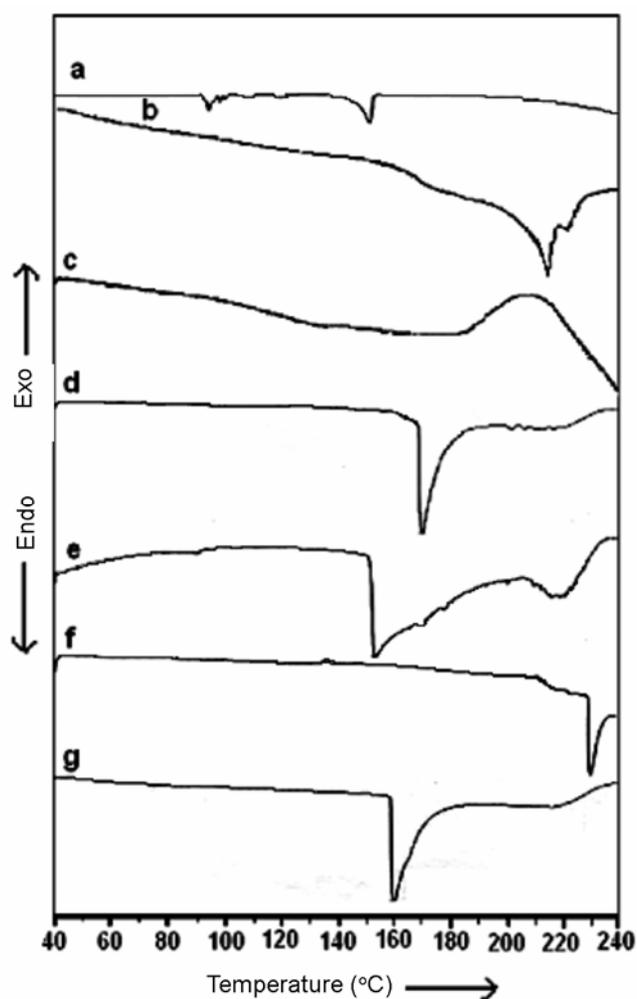


Figure 3. DSC diffractograms of (a) NH_4SCN , (b) PVA, (c) Al_2O_3 nano particles, (d) DMSO casted PVA: NH_4SCN gel electrolyte film and its composite containing (e) 2 wt%, (f) 4 wt% and (g) 6 wt% Al_2O_3 nanofiller.

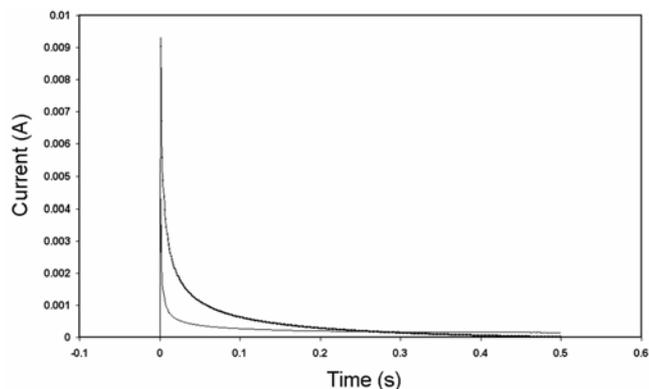


Figure 4. $I-t$ polarization curve of polymer composite electrolytes with (-----) 0 wt% and (\blacklozenge) 6 wt% Al_2O_3 filler.

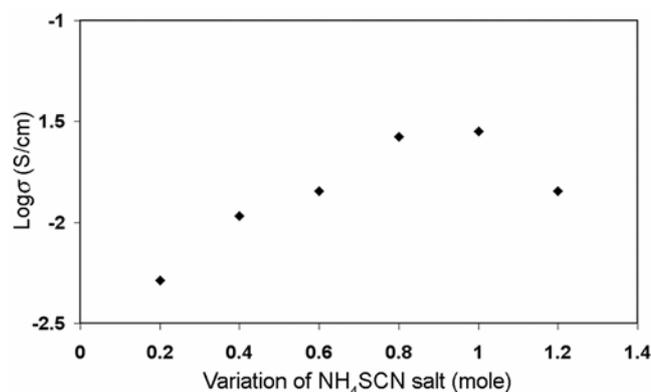


Figure 5. Variation of conductivity of polymer nanocomposite gel electrolytes with NH_4SCN salt concentration (at room temperature).

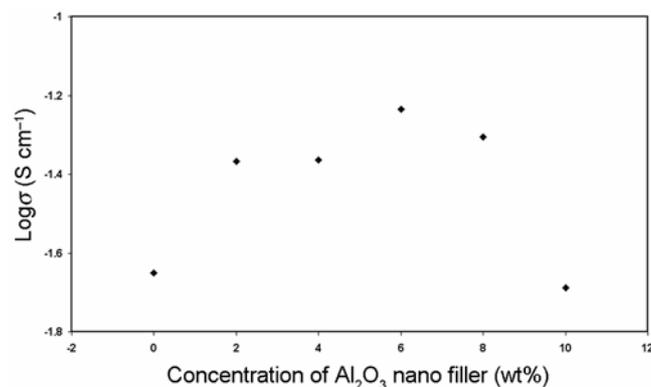


Figure 6. Variation of conductivity of polymer nanocomposite gel electrolytes with Al_2O_3 filler concentration (at room temperature).

polymer. Therefore as the concentration of salt enhances concentration of free ions increases and so the conductivity increases in accordance with the relation:

$$\sigma = nq\mu, \quad (2)$$

where q represents the charge of mobile carrier, n the charge carrier concentration and μ the carrier mobility.

Increase in the amount of salt content leads to increase in fraction of undissociated salt in gel solution. However, the polymer–salt interaction, as reported earlier (Awadhia and Agrawal 2007) and witnessed in XRD studies (figure 2), tends to promote greater dissociation of salt. This is tantamount to higher conductivity values in accordance with relation (ii). For very high salt contents (> 1 M concentration) dissociation of salt by polymer is restricted by further increase in fraction of undissociated salt in gel solution, which raises the viscosity of gel system and hence conductivity decreases.

Figure 6 shows the role of Al_2O_3 nanoparticles concentration on ionic conduction of polymer gel electrolytes. In the presence of filler, conductivity is seen to

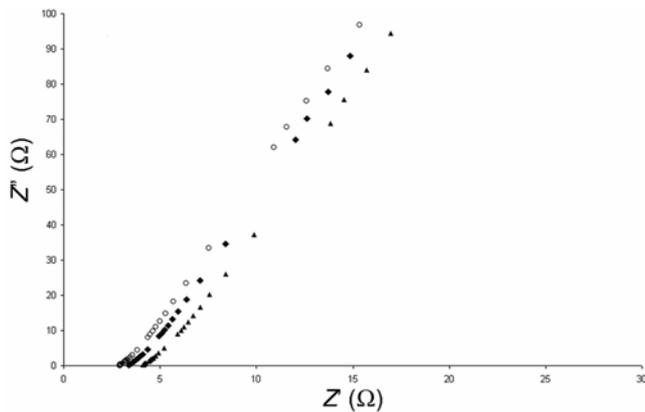


Figure 7. Temperature dependence of the complex impedance spectra of polymer composite electrolytes containing 6 wt% Al_2O_3 nanofiller at (\blacktriangle) 306, (\blacklozenge) 316 and (\circ) 326 K.

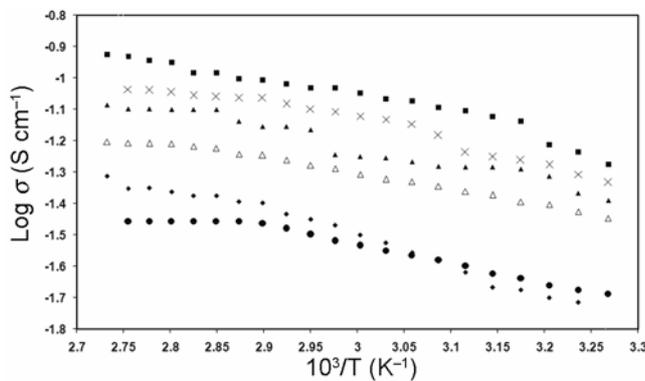


Figure 8. Temperature dependence conductivity of polymer nanocomposite gel electrolytes with (\blacklozenge) 0 wt%, (\blacktriangle) 2 wt%, (Δ) 4 wt%, (\blacksquare) 6 wt%, (\times) 8 wt% and (\bullet) 10 wt% Al_2O_3 filler content.

increase by an order of magnitude. Closer examination of conductivity behaviour shows two maximas, one around 2 wt% and the other around 6 wt% filler concentration – a feature typical of nanocomposite polymer gel electrolytes (Pandey *et al* 2008). At low filler concentration, greater dissociation of salt and increase in amorphous behaviour (XRD studies) tends to enhance free ions concentration and mobility, which significantly enhances ionic conductivity. A flattening in conductivity response is noticed beyond 2 wt% Al_2O_3 contents. This can be associated to the fact that all the salt has been dissociated and so charge carrier concentration is limited. It is only the change in system morphology that tends to affect the conductivity, and thus, again, an enhancement of small magnitude is visible. In situations when there is very large quantity of nanoparticles (beyond 6 wt%) present in the composite system, agglomeration of these nanoparticles takes place, which leads to decrease in conductivity due to creation of tortuous pathways for mobile ions. Another factor that can be associated with the fall in conductivity beyond 6 wt% filler content is the increase in microscopic viscosity of the composite system. Thus, an optimum in conductivity was found (5.81×10^{-2} S/cm) for 6 wt% of Al_2O_3 nanoparticles.

3.6 Temperature dependence of conductivity

Figure 7 shows the temperature dependence of complex impedance spectra of composite gel electrolyte samples, and figure 8 shows the temperature dependence of conductivity of composite gel electrolytes in 1 M NH_4SCN and 5 wt% PVA for different wt% of nano-sized Al_2O_3 . All the curves display similar behaviour, i.e. a combination of Arrhenius and VTF behaviour, with the former being noticed in the low-temperature region and later at higher temperatures. The low-temperature Arrhenius behaviour is on account of the presence of liquid electrolyte encapsulated by the blend matrix, i.e. effect of temperature on conductivity of liquid electrolytes. As the temperature of system is raised beyond 314 K, segmental motion of polymer in polymer composite comes into play and starts affecting the conductivity, leading to VTF nature described by the following relation:

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right), \quad (3)$$

where σ_0 is the pre-exponential factor, B a constant related to activation energy and T_0 ($T_g - 60^\circ$) is quasi-equilibrium glass transition temperature.

A low value of activation energy in low temperature region (table 1) has been observed. Such low values are typically observed for polymer gel electrolytes. Lowering of activation energy till 6 wt% Al_2O_3 content reaffirms improvement in ionic conduction in the presence of nano-sized fillers in polymer gel electrolytes.

3.7 CV studies

Figure 9 compares cyclic voltograms of the PVA gel electrolyte systems having different concentrations of Al_2O_3 nanofiller. It is apparent from this figure that the electrochemical stability is moderately good without any filler which ranges from -1.2 to $+1.4$ V. On addition of the nanofiller, the stability is seen to improve (-1.3 to $+1.4$ V). Another effect of adding the nanofiller is the narrowing of faradic currents during oxidation and reduction cycles in the stable region. A stable potential window is of great practical importance for applications in batteries and super capacitors as it determines the maximum operating voltage of a capacitor (Kubota *et al* 2000, 2002; Kim *et al* 2002). An interesting observation is the appearance of a single oxidation/reduction peak for

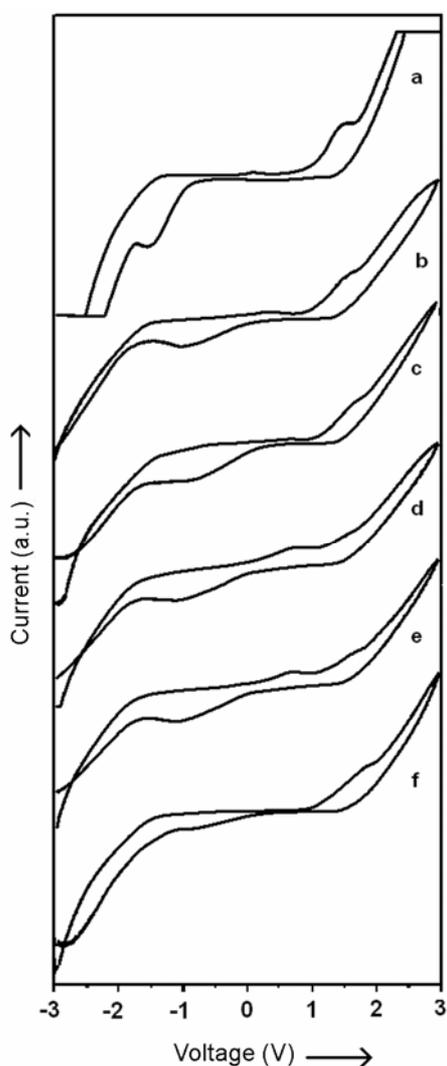


Figure 9. Cyclic voltograms of (a) DMSO casted PVA: NH_4SCN gel film and its composite containing (b) 2 wt%, (c) 4 wt%, (d) 6 wt%, (e) 8 wt% and (f) 10 wt% Al_2O_3 filler content.

all pristine and composite gel electrolytes, which is possibly on account of NH_4^+ ion that contributes to ionic conduction. In the presence of the filler, the reduction peak was noticed to shift on the potential scale along with decrease in the intensity before virtually vanishing in the presence of electrolytes containing 10 wt% filler. These studies indicate improvement in electrochemical stability of nanocomposite gel electrolyte in the presence of Al_2O_3 fillers. Optimum electrochemical window was observed to be ± 1.65 V for composite gel electrolytes containing 6 wt% Al_2O_3 filler.

4. Conclusion

Al_2O_3 nanoparticles-filled polymer gel electrolytes of PVA: DMSO: NH_4SCN have been successfully synthesized by solution cast technique. XRD patterns exhibit broadening of diffraction patterns of composite on addition of Al_2O_3 nanofillers up to 6 wt%, suggesting improved amorphousness. SEM images show formation of uniform dispersed phase in composites. Bulk conductivity of synthesized samples increases by an order of magnitude with increasing amount of Al_2O_3 nanofillers up to 6 wt% of filler content. Maximum absorption of the nanofiller is found to be 6 wt%. Addition of Al_2O_3 nanofillers provides electrochemical current stability to PVA gel electrolyte. All these results indicate possible application of PVA: DMSO: NH_4SCN : Al_2O_3 gel electrolytes in super capacitors, polymer membranes, fuel cells and smart windows. Further studies are underway to establish this.

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