

# Study of Ion Transport Behavior of Nanocomposite Polymer Electrolyte for Battery Application

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#### **Research Article**

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### Abstract

In the present work an attempt has been made to synthesize and characterize polyvinyl alcohol: polyvinyl carbazole (90:10) blend based nanocomposite polymer electrolyte dispersed with SiO<sub>2</sub> namely, (PVA: PVK): CH<sub>3</sub>COONH<sub>4</sub>: EC: SiO<sub>2</sub> system. Improvement in amorphous nature of the system upon addition of SiO<sub>2</sub> nanofillers has been confirmed by XRD and SEM studies. The ionic conductivity of nanocomposite electrolyte improves moderately (~5 times) at room temperature with optimum of  $5 \times 10^{-3}$  S/cm for 6 wt% SiO<sub>2</sub>. The temperature dependent conductivity analysis shows that ion conduction is controlled by combination of Arrhennius and VTF behavior. All the results have been suitably explained. All-solid-state battery has been fabricated in the cell configuration Zn+ZnSO<sub>4</sub> (anode)/polymer Gel Electrolyte (cathode) to establish its practical utility in electrochemical devices. Cell performance studies on cell with 0.4 M electrolyte show open circuit voltage of 1.5 volt with power density 1.12 W/Kg been studied by recording the cell potential discharge profiles at room temperature under different load conditions.

Keywords: Polyvinyl Alcohol; Polyvinyl Carbazole; Nanocomposite Polymer Electrolytes; Polymethyl Methacrylate

### Introduction

In recent past electrochemical based energy storage devices provide a tremendous role in technical applications like computers, communication devices, industrial controls, electric vehicles, laboratory equipments etc. Moreover they have stringent need in the portable electronic market like solar cells, pacemakers, remote controls and even in toys. In these emerging technologies they are having an exclusive demand for long life, environmentally friendly, low cost, reliable rechargeable batteries with specific energy power as expected [1-3]. Within this frame-work polymer electrolytes are materials of great interest for applications in different electro-chemical devices but their relatively poor ionic conductivity limits its utility. The conductivity of these electrolytes is confined mostly in amorphous phase and the crystalline phases are considered as poor conductivity phase. Thus over the years attempts have been made to improve the amorphous phase of polymer electrolyte. Introducing of a plasticizer in small amounts which may be a low molecular weight substance [1], polymer blending [4], using comb- branched copolymer [5], cross- linking of polymer matrices [1] and incorporation of inorganic fillers [6] are the alternative ways to improve the ionic conductivity of polymer electrolyte. Polymer blending is an extensive way to complement advantages of each compartment, improve the electrical behavior and enhance the physical properties of polymer electrolytes. Therefore, blending of polyvinyl alcohol (PVA) and polyvinyl carbazole (PVK) was employed in this work. In general, PVA is solvent swollen character and known to form hydrogels [7,8] and also a potential candidate for development of proton conducting electrolytes. Introduction of PVK in polymer electrolyte is expected to improve the mechanical strength and interfacial properties between electrode and electrolyte [9]. In recent years, polymethyl methacrylate polyacrylonitrile (PMMA) [10-12], (PAN) [13]. polyvinylidene fluoride (PVdF) [11,14] and polyethylene oxide (PEO) [11,15] have been reported as suitable polymer host materials for the preparation of polymer gel electrolyte. The most of the work on polymer gel electrolytes concerns development of lithium- based polymer batteries [11,16-18]. Proton conductors has attracted much attention because of its potential use in clean energy devices such as fuel cell, electrochromic devices (ECDs) and other smart devices [19]. The numbers of fast protonic conductors, organic, crystalline and amorphous, have been prepared during past three decades [3,11,15,20]. Within the realm of polymer gel electrolytes, PVA is also one of the prominent polymer because its good solvent holding capacity and electrochemical stability [7,21] have reported PVA- based proton conducting gel electrolytes with high ionic conductivity.

Generally, poor dimensional, mechanical stabilities and exudation of liquid from gel lump retained for a long period are the main drawback of ionic liquid- based gel polymer electrolytes. Therefore, composite electrolytes are developed to overcome these shortcomings by dispersing the inorganic inert fillers, such as  $SiO_2$ ,  $TiO_2$ and alumina (Al<sub>2</sub>O<sub>3</sub>). Addition of inorganic filler not only improves ionic conductivity but also enhances mechanical stability. In recent times, dispersion of inorganic filler in pristine polymer electrolytes [22] and in polymer blend based electrolytes [23] have been effectively tried to overcome these problems to a great extent leading to formation of nanocomposite polymer electrolytes. Looking into such problems, an attempt has been made in the present work to improve the performance of (PVA: PVK): CH<sub>3</sub>COONH<sub>4</sub>: EC electrolyte system by dispersal of nano- sized SiO<sub>2</sub>. This system is expected to drastically impede crystallization process in polymer based nanocomposite electrolytes and thus improve ionic conductivity. Present system is characterized by using XRD, FTIR, Scanning electron microscopy, electrical measurement and battery fabrication and discharge profile test to evaluate cell performance.

#### **Experimental**

PVA (average molecular weight 124,000- 186,000 Aldrich make), PVK (average molecular weight 40,000 Aldrich make), ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>), AR grade sd fine chem. and aprotic solvent dimethyl Sulfoxide (DMSO) merk limited, were used for synthesis of polymer nanocomposite electrolyte. The preparation of nanocomposite electrolytes involved many steps. First both polymers PVA and PVK were dissolved in DMSO in the ratio of PVA: PVK, 90:10 and stirred for 3 h at 50°C to obtain homogeneous mixing. In the second step an appropriate quantity of ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) salt in EC (Aldrich make) was added to the above mixture to get the composition so as to obtain the polymer blend electrolyte and stirred further for 2h to complete the homogenous mixing. In next step SiO<sub>2</sub> nano filler was mixed in different wt% and stirred for other 2 to 3h. The final solution was poured in poly carbonate pettri dish to obtain thick films of nanocomposite electrolyte system. Silicon oxide (SiO<sub>2</sub>) filler was synthesized by standard solgel technique. Tetraethyl orthosilicate (TEOS) was chosen as precursor material dissolved in a double- distilled water/ethanol mixture for the formation of silicon oxide powder. The pH value of solution was maintain 5-7 with the ammonia solution drops and allowed to gel at 50°C. The gel was dried at 150°C for 12 h followed by thermal treatment at 700°C for 2 h and 900°C for 0.5 h in a kanthal high temperature furnace. The dried material was crushed to obtain fine powder of SiO<sub>2</sub> [24]. C-V and I-t measurements were performed on a CH- electrochemical workstation (CH instruments model CH608) to determine electrochemical window and nature of charge transport. Electrical characterization of the material was carried out using impedance spectroscopy technique. Complex impedance parameters were measured with a Hioki impedance analyzer (model 3520) in the frequency range 40 Hz- 100 KHz using platinum electrodes for electrical contact.

### **Results and Discussion**

#### **XRD Studies**

Figure 1 depicts the XRD pattern of blend based polymer gel electrolyte films of (PVA: PVK):  $CH_3COONH_4$ : EC without and with SiO<sub>2</sub> nanofillers along with pristine components. One relatively sharp characteristic XRD peak at  $2\theta$ = 22.1<sup>0</sup> and a broad peak around 16.7<sup>0</sup> (pattern b) closely matches with the peaks reported for PVK [25]. The slight deviations in characteristic reflection of PVK are possibly due to variation in solvent swollen nature of PVK

in different organic solvents. XRD pattern of as synthesized SiO<sub>2</sub> nanofiller particles showing prominent XRD peak at  $2\theta = 26.6^{\circ}$  (in inset pattern c) to conform to earlier reported results [26]. When the polymer components are admixed together to form PVA:PVK (90:10 ratio) blend the low intensity diffraction peaks appear at 2 $\theta$  values 19.45°. 19.76° and 20.6° while high intensity characteristic reflection is noticed around 24.230 (pattern d). These diffraction maxima occur on account of interaction among components/ intercalation of PVK in PVA leading to formation of a new material viz. polymer blend. It is should be mentioned here that few low intensity peaks are not clearly visible due to merge of different patterns in a single figure. The presence of diffraction peak 19.45° and 19.76° is correlated to existence of un-reacted PVA in the blend. The remaining peaks can be correlated to formation of PVA: PVK blend as they do not correspond to any of the reflection of pristine material. Upon addition of salt CH<sub>3</sub>COONH<sub>4</sub> (pattern e) the XRD peaks of PVK ( $2\theta$ = 16.7°) retraces towards lower  $2\theta$ value. On the other hand, the PVA related peak intensity  $(2\theta = 19.6^{\circ})$  diminishes. Also diffraction peak related to PVA: PVK: DMSO system at 24.2° intensifies owing to enhanced compatibility in the presence of added salt. Recently, PVA has been shown to form complex with ammonium salts leading to formation of polymer gel electrolyte [27-29].

On the same lines it can be argued that ammonium acetate forms complex with linkage at the OH group of PVA. In addition to the XRD peaks appearing at 16.7° and 24.2° few other peaks around 26.9°, 27.2°, 30.6°, 35.2°, 35.7°, 41.1° and 47.6° appear in XRD pattern of composite system. Since none of these peaks are assignable neither to salt nor host polymers it is conjectured that complex formation takes place in electrolyte system. Upon addition of nanofiller  $SiO_2$  (pattern f) all the existing peaks are suppressed with increase in broadening of primary peak except the appearance of a strong sharp peak at  $2\theta = 26.6^{\circ}$ . This peak corresponds to characteristic reflection of SiO<sub>2</sub> according to JCPDS data (file no.461045) and also recorded in the experiment (in inset pattern c). This observation supports the role of SiO<sub>2</sub> as that of passive filler in electrolyte with SiO<sub>2</sub> only improving the morphology of composite blend electrolyte system. Characteristic reflections of nanofiller could not be tracked at higher concentration of SiO<sub>2</sub> due to coverage of SiO<sub>2</sub> particles by matrix electrolyte. The average crystallite size in composite system (Table 1) was also estimated using well- known Debye- Scherrer formula [30] which reflects nano format of electrolyte system in

Kumhar RP. Study of Ion Transport Behavior of Nanocomposite Polymer Electrolyte for Battery Application. Nanomed Nanotechnol 2017, 2(3): 000123. presence of filler particles. Further marginal improvement (decrease in crystallite size) noticed till intake of 6 wt%  $SiO_2$ . As it exceeds a sudden increase in crystallite size is noticed possibly due to agglomeration of nano particles.

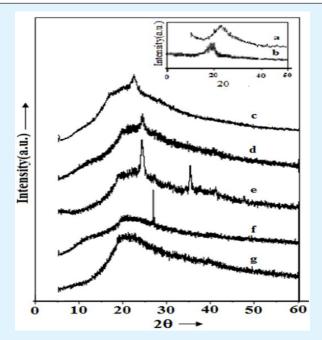


Figure 1: X- ray diffractograms of DMSO casted (c) PVK, (d) PVA: PVK and PVA: PVK:  $CH_3COONH_4$ : EC nanocomposite electrolyte containing (e) 0, (f) 6 and (g) 8 wt% SiO<sub>2</sub>. Inset shows XRD of (a) DMSO casted PVA and (b) SiO<sub>2</sub>.

#### Scanning Electron Microscopy Studies

Figure 2 depicts the surface morphology of DMSO casted PVK, PVA: PVK, PVA: PVK: CH<sub>3</sub>COONH<sub>4</sub>: EC and PVA: PVK: CH<sub>3</sub>COONH<sub>4</sub>: EC: SiO<sub>2</sub> films. In the pure PVK film image plain structure is observed with existence of intermittent pores of small dimension (Figure 2a). In the image of PVA: PVK blend rough surface of irregular pores is observed with cluster of un-dissolved PVK (Figure 2b). The rough surface along with existence of phase separation is an indication of poor compatibility among polymer components as also witnessed during optical microscopy. Upon addition of ammonium acetate salt in PVA: PVK to make polymer blend the original entity is lost and layered type structure with significant decrease in pores size is observed (Figure 2c). This supports better solvent retention capability of electrolyte system. It seems

that there exists better compatibility among polymer components in the presence of salt validating optical microscopic data. Incorporation of SiO<sub>2</sub> filler in mixed conducting system reduces the porosity of system because SiO<sub>2</sub> nanoparticles are entrapped between chains in the pores (Figure 2d). White colored spots observed in the SEM image show that SiO<sub>2</sub> nano filler particles are not fully absorbed.

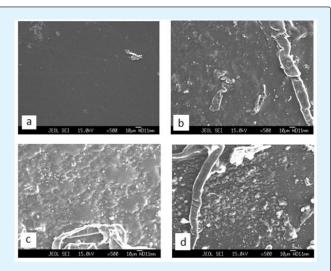


Figure 2: SEM image of DMSO casted (a) PVK, (b) PVA: PVK, (c) PVA: PVK: 0.4M CH<sub>3</sub>COONH<sub>4</sub> and (d) PVA: PVK: 0.4M CH<sub>3</sub>COONH<sub>4</sub>: 6wt% SiO<sub>2</sub>.

#### **DSC Analysis**

DSC thermograms of Figure 3 (i) and (ii) represent the thermal scans for PVA, PVK, PVA: PVK: DMSO and PVA: PVK: CH<sub>3</sub>COONH<sub>4</sub>: EC composite system for two salt molarities (0.4 and 0.6 M) and nanocomposite electrolyte containing 6 and 8 wt% SiO<sub>2</sub> for 0.4 mole salt. Since PVA is known to be partially crystalline material, both characteristic transitions (Tg and Tm) appear in DSC thermogram as evidenced in scan a of Figure 3(i) (T<sub>g</sub>= 88°C and  $T_m$ = 216°C). These transitions are in close agreement with the earlier reported values [27,31]. The glass transition temperature of PVA decreases in the blend and as well as in composite electrolyte system probably due to plasticization of PVA with DMSO used as casting solvent for electrolytes [32]. This transition is observed around 70°C. A broad shoulder peak around 170°C is also evidenced in DSC profile of pure PVA. Such a feature has also been reported earlier [27] and ascribed to phenton melting. In thermogram b of Figure 3(i) glass transitions temperature and melting temperature of PVK

Kumhar RP. Study of Ion Transport Behavior of Nanocomposite Polymer Electrolyte for Battery Application. Nanomed Nanotechnol 2017, 2(3): 000123. appear around 197°C and 337°C respectively, which conform to the result of Cadek et al. [33]. Endothermic transition around 58°C (scan a figure 3 (ii)) shifts toward higher temperature (61°C) upon addition of 0.4 M salt in the blend (scan b of Figure 3 (ii)) and correlated to melting of DMS resulting interaction of DMSO with PVA. It has been shown previously by Agrawal and Awadhia [21,34] that DMSO interacts with PVA and reduces to dimethyl sulfhide (DMS). This endothermic peak is also observed in nanocomposite system containing 6 and 8 wt% SiO<sub>2</sub> at 55°C (scan d) and 49°C (scan e) respectively.

Endothermic transition observed around 221°C in PVA: PVK blend (scan a) can be ascribed to melting temperature of uncomplexed PVA and this peak shifts toward higher temperature upon addition of salt and observed at 223°C and 225°C for 0.4 M (scan b) and 0.6 M (scan c) respectively. Upon incorporation of 6 wt% SiO<sub>2</sub> nanofiller in composite blend containing 0.4 mole ammonium acetate salt, (scan d of Figure 3 (ii)) this peak is shifted to 227°C. On further increasing content of nanofiller this transition retraces back and appears at 217°C. The enthalpy change corresponding to this transition when calculated for electrolyte samples (Table 1) it decreases. However change in enthalpy is minimal for sample containing 6 wt%  $SiO_2$  (26.3 J/g) which is an indication of maximal degree of amorphousness. No transition corresponding to glass transition temperature of PVK (197°C) could be perceived in blend nor their electrolyte. Further multiple endothermic transitions appeared in the temperature range 250°C - 288°C in all electrolytes samples (scan b-e of Figure 3 (ii)) which is attributed to formation of complexes.

Appearance of an endothermic peak around 347°C in PVA: PVK blend can be associated to melting of unblended PVK, and this temperature decreases upon addition of salt due to formation of blend based electrolyte. Upon addition of SiO<sub>2</sub> nanofiller further decrement is noticed in this thermal transition. Moreover the enthalpy change corresponding to this transition is also seen to decrease. A broad endothermic peak in composite system containing 0.4 M salt (scan b of Figure 3 (ii)) is observed around 135°C which can be correlated to melting of PVA: salt complex formed or onset of phenton melting. Since endotherms related to melting temperature of PVA and PVK is observed in all samples in the temperature range 250°C to 288°C, their occurrence suggest formation of partially compatible blend based electrolytes.

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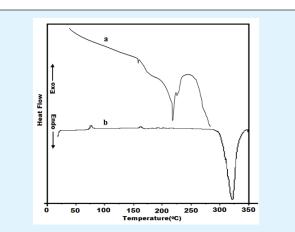


Figure 3 (i): DSC diffractograms (a) PVA and (b) DMSO casted PVK.

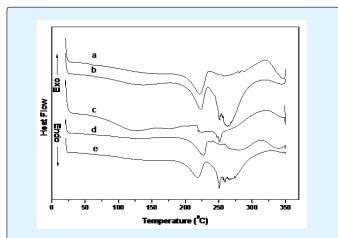


Figure 3 (ii): DSC diffractograms of DMSO casted (a) PVA: PVK, (b) PVA: PVK: 0.4M CH<sub>3</sub>COONH<sub>4</sub>: EC, (c) PVA: PVK: 0.6M CH<sub>3</sub>COONH<sub>4</sub>: EC (d) PVA: PVK: 0.4M CH<sub>3</sub>COONH<sub>4</sub>: 6 wt% SiO<sub>2</sub> and (e) PVA: PVK: 0.4M CH<sub>3</sub>COONH<sub>4</sub>: 8 wt% SiO<sub>2</sub>.

#### Wagner's Polarization

Amperometric I-t technique was used to assess the nature of ion transport and evaluate total ionic transference number from current time plot with platinum electrodes. The variation of current with time for mixed conducting samples is shown in Figure 4. Polarisation behavior is reflected in all these curves. The ionic transference number  $t_{ion}$  was calculated using the relation [35]:

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

Kumhar RP. Study of Ion Transport Behavior of Nanocomposite Polymer Electrolyte for Battery Application. Nanomed Nanotechnol 2017, 2(3): 000123. Where  $I_{\text{ionc}}$  is current due to ions,  $I_{\text{electronic}}$  (or  $I_{\text{final}}$ ) the current due to electrons, and  $I_{\text{total}}$  (or  $I_{\text{initial}}$ ) 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 [36]. The calculated values of  $t_{ion}$  for different composite films varies from 0.9 to 0.8 with varying concentration of SiO<sub>2</sub> filler which ascertains dominance of ionic charge transport over electronic transport in nanocomposite electrolyte.

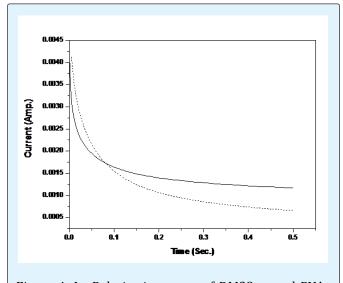
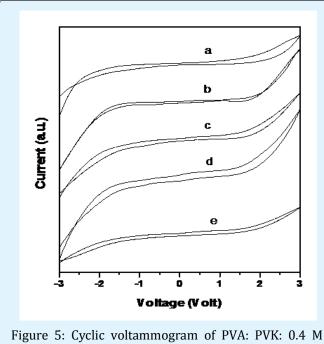


Figure 4: I-t Polarization curve of DMSO casted PVA: PVK: 0.4 M  $CH_3COONH_4$ : EC: SiO<sub>2</sub> containing (solid line) 0 and (---) 6 wt% SiO<sub>2</sub>.

#### **CV Studies**

A stable potential window is of great practical importance for applications of electrolyte materials in batteries and super capacitor [37,38]. Figure 5 compares the cyclic voltagrams of composite electrolyte and nanocomposite electrolyte with loaded different wt% nanofiller of SiO<sub>2</sub>. It is apparent from this figure that electrochemical stability is moderately good without any filler which range – 1.5 V to + 1.6 V. On addition of nano filler stability is seen to improve significantly range from -1.54 V to +1.64V. Another effect of adding the nanofiller is the narrowing of faradic currents during oxidation and reduction cycles in the stable region. An interesting observation is the appearance of a single oxidation/reduction peak for all pristine and composite electrolytes, which is on account of NH4+ ions that contributes to ionic conduction. Oxidation of PVA in presence of DMSO has been envisaged earlier [21]. In the

presences of filler, the reduction peak was noticed to shift on the potential scale along with decrease in the intensity. Comparison of C-V data indicates best cyclic reversibility for composite system containing 6 wt%  $SiO_2$  filler with optimum, improvement in electrochemical stability. Electro chemical window has been found to range from -1.6V to +1.64V.



CH3COONH4: EC:  $SiO_2$  blend based nanocomposite electrolytes containing (a) 0, (b) 2, (c) 4, (d) 6 and (e) 8 wt%  $SiO_2$  nanofiller.

#### **Electrical Conductivity**

The variation of ionic conductivity of composite electrolyte (PVA: PVK): CH<sub>3</sub>COONH<sub>4</sub>: EC system as a function of salt concentration is shown in Figure 6. The conductivity of composite system has been extracted with the help of Cole- Cole plot. The conductivity of composite electrolyte is seen to rise with increasing salt concentration and reach an optimum at 1.27×10-3 Scm-1 for 0.4 M. It has been complex formation takes place in the system, which tends to raise the conductivity of the system through greater dissociation of salts. Dimethyl sulfoxide is highly aprotic solvent and ammonium acetate is likely to dissociate into respective ions at lower concentration and there is nothing to be dissociate. Therefore as the concentration of salt enhances concentration of free ions increases and so the conductivity increases in accordance with the relation:

$$\sigma = nq\mu \dots (2)$$

Where q represents the charge of mobile carrier, *n* the charge carrier concentration and  $\mu$  the carrier mobility. Increase in the amount of salt content leads to increase in fraction of un-dissociated salt in gel solution. However, the polymer- salt interaction, as reported earlier [21]. This in tantamount to higher conductivity values in accordance with relation (2). For high salt concentration > 0.4 M dissociation of salt by polymer is restricted by further increase in fraction of un-dissociated salt in gel solution, which raises the viscosity of gel system and hence conductivity decreases.

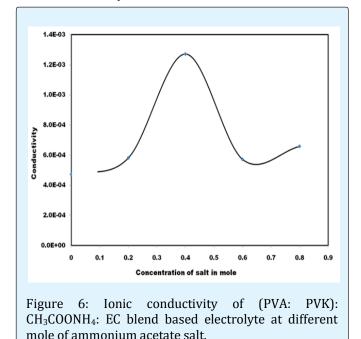


Figure 7 depict the variation of ionic conductivity of nanocomposite polymer electrolyte with SiO<sub>2</sub> filler concentration. The ionic conductivity of nanocomposite electrolyte seen to improves moderately (~5 times) at room temperature for 6 wt% of SiO<sub>2</sub> filler. Close observation of conductivity plot shows two maxima, one around 2 wt% and other around 6 wt% filler concentration- a feature typical of nanocomposite polymer gel electrolyte [26,27]. At low filler concentration, greater dissociation of salt and increase in amorphous behavior tends to enhance free ions concentration and mobility, which significantly enhance ionic conductivity. A flatting in conductivity response is noticed beyond 2 wt% SiO<sub>2</sub> 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 situation when there is very large quantity of nanoparticles (beyond 6 wt%), agglomeration of theses nanoparticles take place, which leads to decrease in conductivity due to creation of tortuous pathways for mobile ions. An another factor that can be associated with the fall conductivity is the increase in the microscopic viscosity of composite system.

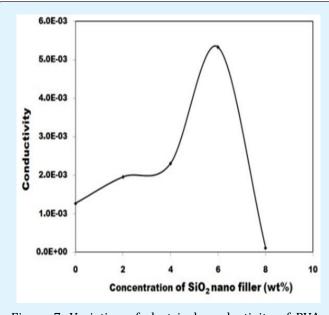


Figure 7: Variation of electrical conductivity of PVA: PVK: 0.4 M CH<sub>3</sub>COONH<sub>4</sub>: EC: SiO<sub>2</sub> blend based nanocomposite electrolyte with different wt% of SiO<sub>2</sub> filler concentration (at room temperature).

#### **Temperature Dependence of Conductivity**

It is clear from Cole- Cole plots of PVA: PVK: CH<sub>3</sub>COONH<sub>4</sub> system that there is a continuous drop in bulk resistance of composite system with increase of temperature. Hence temperature dependence of electrical conductivity of (PVA: PVK): CH<sub>3</sub>COONH<sub>4</sub>: EC: SiO<sub>2</sub> system at different filler concentration was studied and the result have been shown in Figure 8. The variation of conductivity indicates that the conductivity increases with rise in temperature with two distinct straight lines separated by a region in which there a non-linear change in conductivity value. At low temperature (around room temperature) the conductivity response is essentially dictated by the trapped liquid electrolyte within the polymer matrix and hence Arrhenious behavior is

noticeable. However, as the temperature approaches the glass transition temperature of polymer PVK (65°C) in polymer composite system, the matrix becomes flexible giving rise to conductivity response associated to that PVA: CH<sub>3</sub>COONH<sub>4</sub> electrolyte. Therefore as the temperature is raised further the conductivity enhancement is best described by VTF relationship. All the curve display similar behavior i.e. combination of Arrhenius and VTF with former being noticed in the low-temperature region and later at higher temperatures.

$$\sigma = \sigma_0 \exp\left(-E_a / KT\right) \tag{4}$$

$$\sigma = \sigma_0 T^{-1/2} \exp\left(-E_a / T - T_0\right)$$
(5)

Where  $\sigma_0$  is the pre-exponential factor, the activation energy and  $E_a$  is activation energy *K* is the Boltzmann constant and  $T_0 = T_g - 60^{\circ}C$  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.

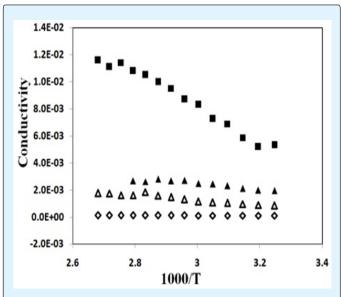


Figure 8: Temperature dependent conductivity of PVA: PVK: 0.4M CH<sub>3</sub>COONH<sub>4</sub>: EC: SiO<sub>2</sub> blend based nanocomposite electrolytes with ( $\triangle$ ) 0, ( $\blacktriangle$ ) 2, ( $\blacksquare$ ) 6 and ( $\diamondsuit$ ) 8 wt% SiO<sub>2</sub>.

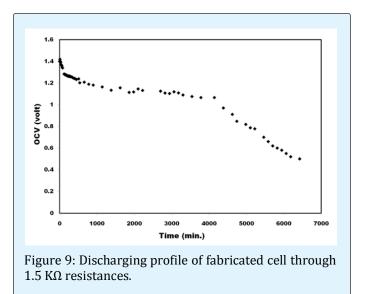
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S. No.	Samples Name	Average Crystallite Size(nm)	Change in enthalpy (J/g)	Ionic transference number t <sub>ion</sub>	σ <sub>dc</sub> (S/cm)	Activation energy E <sub>a</sub> (ev)
1	PVA: PVK: DMSO	~35.38	30	-	-	-
2	PVA: PVK: 0.4 m CH <sub>3</sub> COONH <sub>4</sub>	~33.16	28.2	0.7	1.27x 10 <sup>-3</sup>	0.47
3	PVA: PVK: 0.6 m CH <sub>3</sub> COONH <sub>4</sub>	~32.5	27.3	-	-	-
4	PVA: PVK: 0.4 m CH <sub>3</sub> COONH <sub>4</sub> : 2wt% SiO <sub>2</sub>	-	-	0.93	1.96 x 10 <sup>-3</sup>	0.3
5	PVA: PVK: 0.4 m CH <sub>3</sub> COONH <sub>4</sub> : 4wt% SiO <sub>2</sub>	-	-	0.82	2.31 x 10 <sup>-3</sup>	0.2
6	PVA: PVK: 0.4 m CH <sub>3</sub> COONH <sub>4</sub> : 6wt% SiO <sub>2</sub>	~30.20	26.3	0.9	5.33 x 10 <sup>-3</sup>	0.086
7	PVA: PVK: 0.4 m CH <sub>3</sub> COONH <sub>4</sub> : 8wt% SiO <sub>2</sub>	~118.2	28.9	0.46	1.13 x 10 <sup>-4</sup>	0.138

Table 1: Average crystallite size, Change in enthalpy, Ionic transference number and activation energy of some samples.

#### All-Solid -State Battery

Looking into wide temperature and electrochemical window of the nanocomposite electrolytes all-solid state battery has been fabricated using PVA: PVK: 0.4M CH<sub>3</sub>COONH<sub>4</sub>: EC: SiO<sub>2</sub> as electrolyte to test the utility of electrolytes in battery application. All solid state battery was designed in the configuration (Zn+ZnSO<sub>4</sub>) || PVA: PVK: 0.4M CH<sub>3</sub>COONH<sub>4</sub>: EC: SiO<sub>2</sub>|| (C+V<sub>2</sub>O<sub>5</sub>+Electrolyte) and subjected to discharge profile test to evaluate cell performance. Open circuit voltage (OCV)  $\sim 1.5$  V has been obtained for the cell. The Cell was discharged through load resistance  $1.5 \text{ K}\Omega$  at room temperature. Initial drop in the potential followed by a plateau region and ultimate fall in cell voltage is observed (Figure 9) with 1.5 K $\Omega$  load resistance. The cell potential discharge profile is shown in Figure 9 Some important parameters, calculated in the plateau region of the discharge profile are listed in Table 2. The observed favorable results clearly outline the importance of these blend electrolyte in solid state battery applications.



Maximum OCV (Volt)	Working Voltage (Volt)	Current (I) mA	Electric Power (P) mW	Electric Energy (E) mWh	Current Density (J) mA cm <sup>-1</sup>	Power Density W/Kg	Energy Density Wh/Kg
1.42	1.13	0.75	0.85	39.29	0.45	0.85	39.29

Table 2: Some important cell parameters calculated in the plateau region of the cell potential discharge profile.

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