

Research Article

STRUCTURAL AND IONIC TRANSPORT STUDY OF NATURALLY PLASTICIZED NANO-POLYMER ELECTROLYTE FOR DEVICE APPLICATION

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ABSTRACT

Objective: Polyvinyl alcohol (PVA) is a most common biodegradable polymer. The polymer salt interaction in the presence of a natural plasticizer opens the important route for the device application.

Experiment: This development of the composite membrane with the phase inversion technique is a better option. The characterization of the membrane with different experimental techniques like XRD, IR, and Impedance measurements were done.

Result: The developed membrane shows the semi-crystalline nature. It also confirms the plasticization of the polymer matrix modify the basic structural morphology of the polymer matrix. The FTIR study shows the polymer salt interaction in the presence of aloe-vera. The membrane shows the relatively high and almost temperature-independent ionic conductivity of the order of 10^{-4} S/cm.

Conclusion: The plasticized polymer salt composite shows a novel behavior for the new device application like rechargeable solid-state battery as well as PEMC.

Keywords: Poly-venyl alcohol (PVA), Aloe-vera gel (AV), natural plasticizer

INTRODUCTION

It is well known that solid electrolytes are promising conducting materials due to their high value of conductivity comparable to that of liquid electrolytes. In order to fabricate a high conducting polymer membrane, the infusion of a natural gel within a polymer as Poly (vinyl alcohol) (PVA) has become a wonderful choice. PVA is a biodegradable synthetic polymer having high dielectric constant, hydrophobicity, good optical properties, cost effective and non-toxic. It is readily soluble in both water and DMSO. However, its solubility in a mixture of DMSO-water is highly dependent on the solvent composition. Because of the strong interaction of water with DMSO, the PVA solutions were influenced by the composition of the binary solvent mixture. DMSO is a high melting, polar and aprotic solvent widely used in organic and inorganic chemistry. It serves as a H-atom acceptor in hydrogen bonding and is used as an ambidentate ligand in coordination chemistry. The evaluation of the influence of intermolecular interactions on the internal structural parameters of the chemically bonded DMSO molecules affords precise structural data of the free molecule as a point of reference [1]. An another important aspect of residual DMSO in PVA film is that it acts as plasticizer, lowering the T_g and thus improving segmental motion of polymeric chains and should have impact on the ionic conductivity [2]. In the case of polymer electrolytes, its solvent free nature becomes the main advantages due to the significant reduction in the electrolyte thickness with respect to liquid electrolytes. The reduced thickness allows one to decrease the internal resistance of a battery, at the same conductivity level. It means that polymer electrolytes provides both safety and better performance in addition to high conductivities and a wide enough electrochemical window, good electrochemical stability, high thermal and mechanical performances. Moreover, amorphous character for polymer electrolytes was assumed to have better ionic conductivity [3,4] and later it was confirmed by NMR investigations that conductivity predominates in amorphous phases, where ion mobility is chain-assisted.

So the solid polymer electrolytes (SPE) due to their potential applications in solid-state electrochemical devices and in particular in solid-state rechargeable lithium batteries are gaining much impetus. These polymer lithium ion batteries are drawing

considerable attention for their potential applications in personal communication equipment, small portable electronic and electric vehicles [5-9]. It has many advantages, namely high ionic conductivity, high specific energy, a solvent free condition, wide electrochemical stability windows, light and easy processability. Solid polymer electrolytes can be used as electrolytes as well as separator between the electrodes. These have advantages over liquid ones, as there is no problem of leakage of electrolyte [10-13]. In most SPE, in order to enhance the conductivity the polymer host is doped with inorganic salts. The dissociation of inorganic salts introduces ionic mobility which in turn enhances the conductivity of the membrane which might have occurred primarily through the solvents [14]. Aloe vera is known from since time immemorial as the oldest therapeutic herb. It consists of two important parts in which the outer layer is called vascular bundle and the inner layer is known as colourless parenchyma containing aloe vera gel. Aloe vera has three compositions that include structural, chemical as inorganic compounds, and small organic compounds including polysaccharide. These polysaccharides have phenolic-OH which plays important role in conductivity [15-17]. Natural plasticizers (like AV) are biodegradable. PE is less studied for the device applications.

The present work has been done to develop an environmental friendly natural plasticizer based polymer electrolyte. For that we have fabricated the polymer composite membrane by solution cast technique, and studied the effect of plasticizer on its structural and ionic behaviour using the different experimental tools.

MATERIALS AND METHODS

Composite polymer electrolyte films $x(\text{PVA-AV})$: $(1-x)\text{LiSCN}$ were prepared using solution cast technique. Polyvinyl alcohol (PVA - Mw: 85000-124000, ACROS organics) and lithium thiocyanate (Rankem India, AR grade) were used to synthesize the composite electrolyte. Polymer and salt both are dissolved in a common solvent DMSO. The extracted Aloe Vera gel was mixed stoichiometrically in prepared polymer salt solution. To get aloe gel, leaves were collected and processed from a single garden plant. The process of gel extraction is described earlier. The gelatinous

polymeric solution was finally casted in a polypropylene petri dish. This film was dried in controlled atmosphere, followed by vacuum drying to obtain the solvent free standing film. The structural behaviour of the fabricated films were then studied by X-ray diffractometer (Phillips X-pert model) in the Bragg's angle (2θ) $15-60^\circ$ using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$). Polymer salt interactions and complexation behaviour were studied by infrared spectrogram (Bruker Alpha FTIR spectrophotometer, Germany). The electrical characterization of the fabricated polymer composite film was carried out using Impedance spectroscopy (HIOKI LCR Hi Tester, model 3522, JAPAN) by applying small a.c. signal ($\sim 20\text{mV}$) across the sample cell with Pt-blocking electrode.

RESULTS AND DISCUSSIONS

XRD studies

Fig-1 shows the XRD pattern of [50PVA + 50 AV] and $[x(50\text{PVA} + 50\text{AV}) - (1-x)(\text{LiSCN})]$ [$x = 5\%$, 10% , and 25%] complexed polymer electrolyte films. The XRD pattern of (50PVA + 50 AV) exhibits two significant sharp peaks at $2\theta = 19.36^\circ$ and 20.10° . Broad humps with some low peaks were also observed. This confirms the semi-crystalline nature of the composite film. The comparative studies of XRD pattern reveal that when LiSCN salt is incorporated in the polymer matrix, the intensities of main peaks decreases with an increase in the broadness of the peak suggests an increase in the amorphicity of the polymer electrolytes. This could be due to the disruption of the semi-crystalline structure of the polymer by salt dissolution. XRD pattern also shows clearly that the plasticization of the polymer matrix affect the intensity of the characteristics peaks of PVA.

FTIR Studies

Fig-2 shows the FTIR spectra of the host polymer interactions with composite electrolyte. The spectra of composite explain the interaction of polymer/AV/salt on the basis of -

- PVA has a broad peak at 3300cm^{-1} assigning as -OH stretching. The intensity of the same peak drastically enhanced after the plasticization with AV, since AV has

maximum water content ($\sim 92\%$) of its total constituent. Similar effect is observed at 1660cm^{-1} peak which is also related to -OH binding.

- PVA has twin peaks at 2910cm^{-1} and 2850cm^{-1} belong to the symmetrical mode of $\text{V}_s(\text{CH}_2)$ and $\text{V}(\text{CH})$ vibrations, after plasticization. The first peak splits into a doublet and the second peak intensity decreases. The effect of intermingling carbonyl group of AV with PVA is clearly seen as the $\text{C}=\text{O}$ stretching at 1728cm^{-1} and 1707cm^{-1} merge in a single peak with higher intensity. The characteristic peak of amino acid present in AV is visible separately at 1640cm^{-1} in the spectra. The other characteristic peaks of PVA i.e. at 1565cm^{-1} ($\text{C}=\text{O}$ stretching), 1240cm^{-1} [$\text{V}_w(\text{CH})$], 114cm^{-1} [$\text{C}-\text{C}$ and $\text{C}=\text{O}$ stretching], 846cm^{-1} [$\text{C}-\text{C}$ stretching $\text{V}(\text{C}-\text{C})$] and 611cm^{-1} [out of plane -OH bending] present in the spectra. The new peaks or increase in the intensities of the peaks after plasticization is a clear indication of the interaction/modification of the polymeric matrix. Some new peaks, related to amino acid present in AV present at 1420cm^{-1} and 1366cm^{-1} with 1315cm^{-1} belong to the stretching of NO_2 which is characteristics of the aromatic nitro group. After the dispersion of the salt, lithium thiocyanate, a prominent peak at 2055cm^{-1} is appeared, which is a characteristic peak of LiSCN.
- Peak at 2931cm^{-1} is assigned as C-H stretching (DMSO). The peaks at 1435cm^{-1} and 1311cm^{-1} are attributed to antisymmetric bending of CH_3 and symmetric deformation of CH_3 group respectively of solvent DMSO. On the addition of DMSO to LiSCN, the peak at 1311cm^{-1} got appreciably shifted to 1316cm^{-1} . The stretching frequency at 1053cm^{-1} corresponding to $\text{S}=\text{O}$ of DMSO is shifted to the lower wave number side due to the interaction with polymer (i.e. cation) chain. The appearance of peak at 706cm^{-1} band in composite electrolyte shows the interaction of SCN^- with DMSO. As we know that at 701cm^{-1} , the C-S stretching frequency is of pure DMSO.

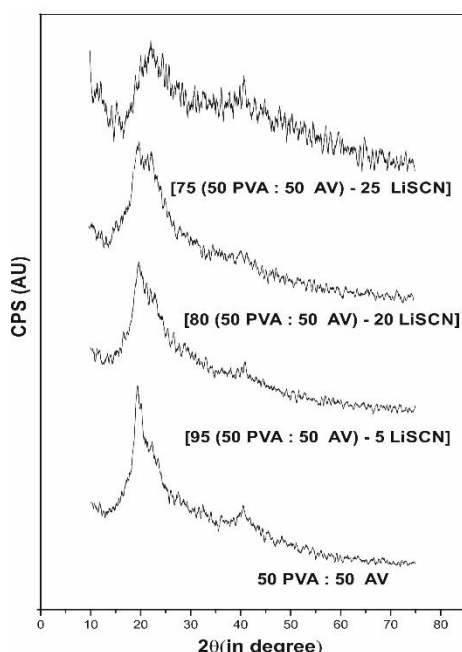


Fig.1: XRD pattern of Different electrolytes

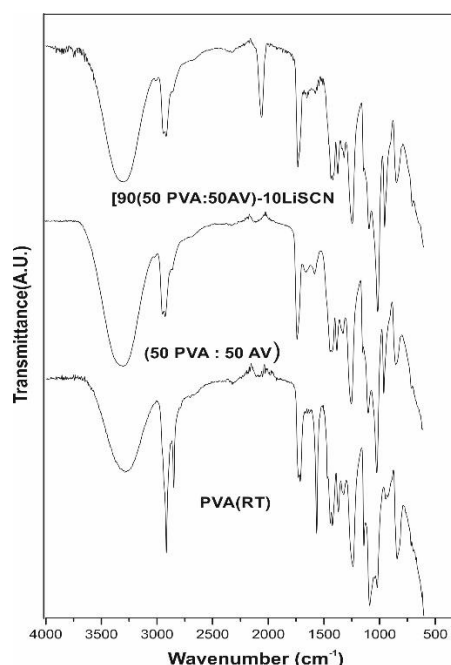


Fig. 2: FTIR study of different polymeric membrane

The IR spectra at different annealing temperatures do not show any drastic changes in the peak positions. This indicates that interactions remain unchanged even at varying temperatures. The

increase in the area and intensities of some peaks is due to the change in the vibrations with the temperature.

Ion Transport/Conductivity Studies

The composition dependence study shows that the maximum conductivity is 1.2×10^{-3} S/cm for the composition [90(50PVA: 50AV) – 10 LiSCN]. To check the thermal window of fabricated composite membrane, we have recorded the variation of conductivity with temperature. The temperature-dependent conductivity is shown in Fig-3. The variation of conductivity with temperature show almost constant in a limited temperature range (i.e., RT- 100°C). After this, a small decrease in conductivity was observed. This decrease is due to the dehydration of the PVA/AV. Final decrease in conductivity is due to the evaluation of lithium-ion from the salt.

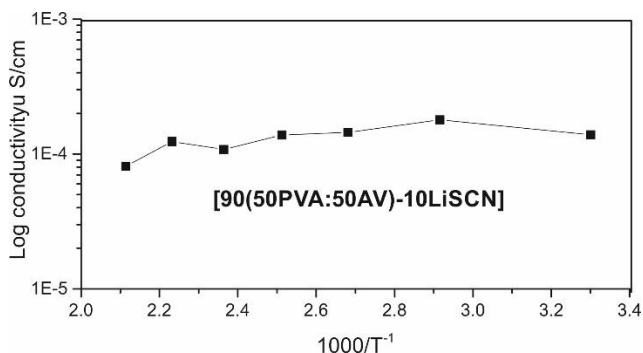


Fig.3: Temperature dependence conductivity of Electrolyte

CONCLUSION

The synthesized composite membrane shows the semi-crystalline nature. The modification in the basic structural morphology of the polymer matrix is observed due to its plasticization. Randomly interwoven nano-fibrous structures are generally preferred for electrolyte systems due to their continuous structure. The use of nano-filler provided better polymer interface as well as the high free volume size, through which molecules transport occurs in the nano-composite membrane matrix. The advantage of a surface

comprised of ultra-fine, continuous nanofibers naturally becomes highly porous. The high porosity is the major responsive factor to enhance the ionic conductivity which was determined through impedance study in the temperature range 298-373 K. The FTIR study clearly shows the polymer salt interaction in presence of aloe-vera. The membrane shows the relatively high and almost temperature-independent ionic conductivity of the order of 10^{-4} S/cm. The plasticized polymer salt composite shows a novel behavior for the new device application like rechargeable solid state battery as well as PEMC.

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