



STRUCTURAL AND ELECTRICAL STUDIES ON BLEND BASED POLYMER GEL ELECTROLYTES

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ABSTRACT

In the present study an attempt has been made to cast a stable free standing PVA: PVP blend based polymer gel electrolyte film using ammonium acetate salt ($\text{CH}_3\text{COONH}_4$) and characterize them for application in solid state batteries. Formation of blend as well as composite polymer electrolyte is confirmed by XRD studies. Ionic conductivity of PVA: PVP blend based polymer gel electrolyte, namely, PVA: PVP: $\text{CH}_3\text{COONH}_4$ is seen to improve by an order of magnitude at room temperature with an optimum 1.34×10^{-3} S/cm for 0.4 mole ammonium acetate concentration. I-t measurement ($t_{\text{ion}} \sim 0.9$) establish dominance of ionic charge transport in synthesized electrolytes. Combination of Arrhenious and VTF behavior is reflected during temperature dependent conductivity analysis. Jonscher Power law seems to be obeyed according to ac conductivity measurement.

Keywords: Polymer Gel Electrolyte, XRD, Ionic Conductivity, Ionic Transport Number

INTRODUCTION

Polymer electrolytes have become materials of great importance for use in different electrochemical devices due to their unique properties like ease mouldability into any shape, light weight, flexibility adhesive property and good electrode- electrolyte contact. However these polymer electrolytes exhibit low ionic conductivity in comparison to liquid electrolytes [1-2]. Over the years, a number of approaches have been tried to augment the ionic conductivity to attain a value close to that of liquid electrolytes [3]. Blending of two polymers leading to formation of blend based polymer gel electrolyte has emerged as one of the attractive way for conductivity improvement in polymer electrolytes [4]. Among the various host polymers used in electrolyte development, PVA exhibits excellent physical properties such as mechanical strength, electrochemical stability, non toxicity, good film forming capability and biocompatibility [5]. Further, it is a semicrystalline polymer where crystalline behavior can be suppressed by addition of amorphous natured PVP to great extent [6]. Further PVA based gel electrolyte system with ammonium salt has been shown to yield high electrical conductivity [7]. Prompted by these considerations, an attempt has been made in the present work to synthesize PVA: PVP blend based electrolyte namely, PVA: PVP: $\text{CH}_3\text{COONH}_4$ system and characterize their free standing films using XRD, electrochemical measurements and conductivity

measurements for device applications namely, solid state batteries.

EXPERIMENTAL

PVA (average molecular weight 124,000- 186,000 Aldrich make), PVP (average molecular weight 360,000 Aldrich make), ammonium acetate ($\text{CH}_3\text{COONH}_4$), AR grade sd fine chem make and aprotic solvent dimethyl sulphoxide (DMSO) Merk make, were used for synthesis of blend based polymer electrolyte. Both polymers PVA and PVP in the ratio (PVA: PVP) of 80:20 were dispersed in different molar salt solution of $\text{CH}_3\text{COONH}_4$ in DMSO and stirred for 8-10 h at 50°C to attain homogeneous mixing. The final viscous solution was poured in a poly carbonate petri dish to obtain thick films of blend based electrolyte. Morphological behavior of as synthesized composite films was studied using XRD (RIGAKU JAPAN MINIFLEX-II in the range $2\theta = 5^\circ$ to 70° with wavelength $\lambda = 1.5406 \text{ \AA}$). 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 electrolyte sample 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 at different temperatures using platinum electrodes for electrical contact.

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RESULT AND DISCUSSION

XRD Studies

Figure 1 depicts the XRD pattern of DMSO casted PVA, PVP, PVA: PVP blend and PVA: PVP: $\text{CH}_3\text{COONH}_4$ complex for different salt concentrations. In the diffraction pattern of DMSO casted PVA gel film (inset a of fig 1) two convoluted peaks at $2\theta = 19.6^\circ$ and 21.8° are observed. The characteristic peak at $2\theta = 19.6^\circ$ corroborates the result

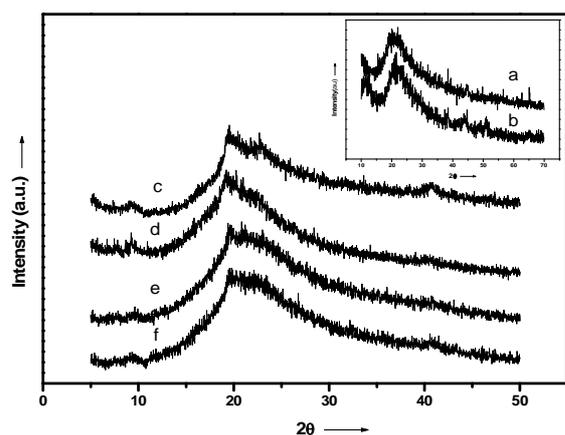


Fig. 1. XRD pattern of DMSO casted PVA: PVP: $\text{CH}_3\text{COONH}_4$ blend based electrolyte containing (c) 0, (d) 0.2, (e) 0.4 and (f) 0.6 M $\text{CH}_3\text{COONH}_4$ salt. Inset shows XRD pattern of (a) DMSO casted PVA and (b) PVP

of Awadhia and Agrawal [8]. Broad XRD peaks located at $2\theta = 11^\circ$ and 22° in diffractogram (inset b of fig. 1) correspond to PVP. Also, secondary reflections (relatively broad) observed at 44.7° and 51° (on 2θ scale) ascertain polycrystalline/semi-amorphous nature of the polymer. When the two polymer components are added to form PVA: PVP blend (80: 20 ratio), the characteristic peak of PVA shifts toward lower diffraction angle (19.44°) and characteristic peak related to PVP shifts toward higher 2θ value at 22.72° fig. 1(c). Further 44.7° and 51° diffraction peaks vanish and a new peak is observed around 40.8° . These observations suggest formation of new material viz. PVA: PVP blend. In the diffraction pattern of PVA: PVP: $\text{CH}_3\text{COONH}_4$ blend based electrolyte (curve d, e, and f) the characteristic peaks of PVA (19.6°) and PVP (22°) seen to merge and result in a broad peak centered around $2\theta = 19.18^\circ$. The broadening of peak signifies enhanced amorphous nature of gel film. The broadening of intense peak can be correlated to the presence of excess liquid trapped within polymer blend matrix. It is being further

noticed that as the fraction of salt in electrolyte increase, there is a small variation in the value of 2θ corresponding to characteristic peak of blend with increasing broadness which signifies change in the morphology of system.

Wagner's Polarization

The total ionic transport number (t_{ion}) was evaluated using the well known d.c. polarization technique [9]. In this technique, as synthesized blend electrolyte samples were polarized by applying a step potential across cell configuration SS| electrolyte |SS and the resulting potentiostatic current measured as a function of time. The variation of current with time for electrolyte samples is shown in figure 2. Polarisation behaviour is reflected in all these curves as per expectation

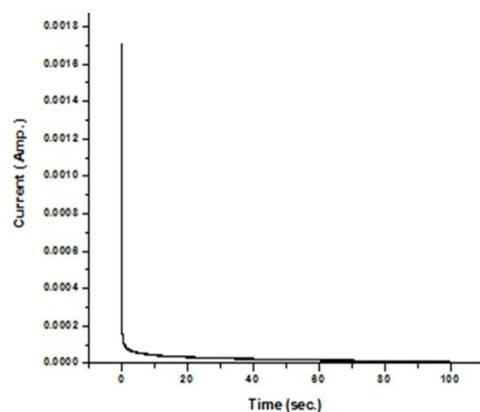


Fig. 2. I-t polarization curve of DMSO casted PVA: PVP: $\text{CH}_3\text{COONH}_4$ blend based polymer electrolyte containing 0.4 mole of salt.

The calculated values of t_{ion} for different composite films varies from 0.9 to 0.96 with varying molar concentration of salt which ascertains predominance of ionic charge transport over electronic transport in polymer electrolyte samples.

Electrical Conductivity

The ionic conductivity of blend based electrolyte for different wt% of PVP at 0.4 mole $\text{CH}_3\text{COONH}_4$ concentration is shown in figure 3. The conductivity of electrolyte increases upon increasing the PVP content till 20 wt% and thereafter it falls till 30 wt% followed by a flattening between 30 to 40 wt%. When PVP content in blend exceeds 40 wt% conductivity finally decreases rapidly. The initial rise of ionic conductivity can be described by the argument that as PVP (< 20 wt%) is introduced in pristine electrolyte,

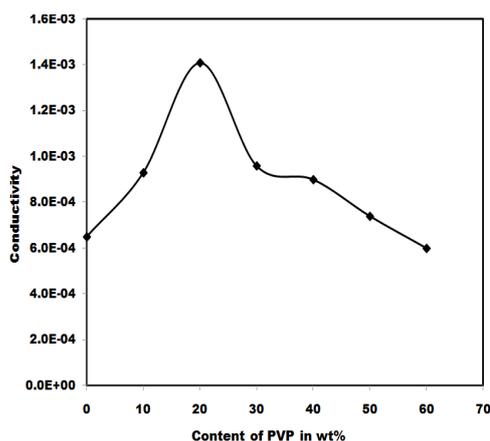


Fig. 3. Ionic conductivity of blend based electrolyte for different wt% of PVP at 0.4 mole $\text{CH}_3\text{COONH}_4$ concentration.

interaction among polymer component takes place leading to improvement in compatibility and morphology of system in the presence of salt. Subsequently formation of PVA-PVP- $\text{CH}_3\text{COONH}_4$ -DMSO complex take place. Improvement in morphology leads to enhancement in mobility of the system. Simultaneously greater dissociation of salt takes place in the presence of improved compatibility which coerces greater dissociation of salt (increase in carrier concentration). Both these factors tend to increase the overall conductivity response. However, on increasing the concentration of PVP beyond 20 wt% viscosity of system is increased thereby creating tortuous pathways for ion migration which causes ionic conductivity to diminish in accordance with Walden's rule. Flattening between 30-40 wt% PVP content in blend can be rationalized by breathing chain model. According to this model polymer chain breathes while it opens up or folds, occupying different volumes in the process. This leads to localized pressure change or fluctuation in surrounding volume. The localized turbulent pressure wave can either assist in dissociation of the ionic pair resulting in an increase in number of mobile charge carrier ions or in enhancing mobility. In either case, ionic conductivity of gel electrolyte is bound to augment which tends to counterbalance the viscosity effect. When PVP content is enhanced further, viscosity effect again dominants leading to fall in conductivity.

Temperature Dependence of Conductivity

Temperature dependence of electrical conductivity of PVA: PVP: $\text{CH}_3\text{COONH}_4$ system at different salt

concentration was studied and the results have been shown in figure 4. The variation of conductivity is seen to change slowly with temperature. At low temperature (around room temperature) the conductivity response is essentially dictated by the trapped liquid electrolyte within the polymer matrix and hence Arrhenius behavior is noticeable. However, as the temperature approaches the glass transition temperature of polymer PVA (75°C) in polymer composite system, the matrix becomes flexible giving rise to change in conductivity values. The enhancement in conductivity with increasing temperature can be rationalized with free volume model. The behavior of conductivity at 0.2 mole shows combination of two Arrhenius curves. As the salt concentration enhances the overall behavior is best described by combination of Arrhenius and VTF behavior and finally at high concentrations (0.6 M) the behavior becomes VTF type.

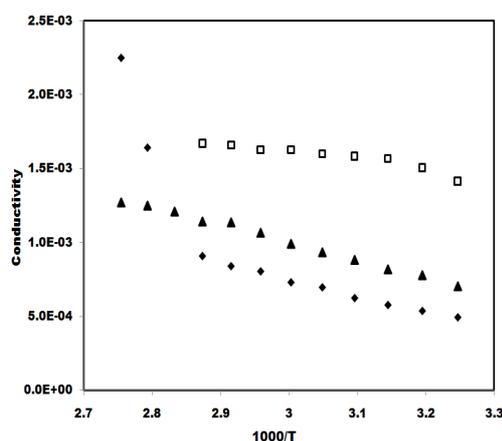


Fig. 4. Temperature dependence electrical conductivity of PVA: PVP: $\text{CH}_3\text{COONH}_4$ system at (♦) 0.2, (□) 0.4 and (▲) 0.6 mole Ammonium acetate concentration.

A.C. Conductivity

Figure 4 shows the variation of a.c. conductivity of blend based electrolyte for different salt molarties. It is apparent from fig that a.c. conductivity increases with frequency in the low frequency regime followed by a nearly frequency independent behavior at high frequencies. The increasing conductivity behavior is connected to the electrode- electrolyte phenomena, and attributed to the space charge polarization at the blocking electrode while saturation like behavior results from failure of hopping of ions from one side to another with increasing frequency.

