CHAPTER 5
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Electrical Conductivity Studies on Ammonium Bromide Incorporated With Zwitterionic Polymer Blend Electrolyte for Battery Application

5.1 Abstract

Solid polymer blend electrolytes are widely studied due to their extensive applications particularly in electrochemical devices. Blending polymer makes the thermal stability, higher mechanical strength and inorganic salt provide ionic charge carrier to enhance the conductivity. In these studies, 50% polyvinyl alcohol (PVA), 50% poly (N-vinyl pyrrolidone) (PVP) and 2.5% L-Asparagine mixed with different ratio of the ammonium bromide (NH₄Br), have been synthesized using solution casting technique. The prepared PVA/PVP/L-Asparagine/doped-NH₄Br polymer blend electrolyte films have been characterized by various analytical methods such as FT-IR, XRD, impedance spectroscopy, TG-DSC and scanning electron microscopy. FT-IR, XRD and TG/DSC analysis revealed the structural and thermal behaviour of the complex formation between PVA/PVP/L-Asparagine/doped-NH₄Br. The ionic conductivity and the dielectric properties of PVA/PVP/L-Asparagine/doped-NH₄Br polymer blend electrolyte films were examined using impedance analysis. The highest ionic conductivity was found to be 2.34×10⁻⁴ Scm⁻¹ for the m.wt. composition of 50% PVA: 50% PVP: 2.5% L-Asparagine: doped 0.15 g NH₄Br at ambient temperature. Solid state proton battery is fabricated and the observed open circuit voltage is 1.1 V and its performance has been studied.

5.2 Introduction

The biodegradable polymers play a vital role and variety of technological applications for the improvement of advanced batteries, catalyst, fuel cell, sensors, Electro chromic display device and drug delivery system [108, 129, 155-160]. Proton or ionic conducting polymer electrolytes have been applied much attention due to their essential role in electrochemical equipment like cells and batteries [161]. The research has been carried out for the development of polymer-blended electrolytes towards battery applications [15, 162-164]. The batteries consists of solid polymer electrolytes because of their properties like cost effective, comfortable with safe under various conditions, environmental
friendly and produce endless design, flexible high performance [26, 94-97]. Polyvinyl alcohol (PVA) is low cost, non-toxic, eco-friendly and chief synthetic polymers due to their high dielectric strength, high velocity of charge transfer in electrode-electrolyte interface and finds applications in numerous fields [103, 105, 165].

The PVA is well known semi crystalline polymer with ionic conductivity 2.5 × 10^{-10} \text{Scm}^{-1} [166]. It is the excellent biomaterials, low cost and non-carcinogenic in nature [167]. Poly(N-vinyl pyrrolidone) (PVP) is an amorphous polymer which exhibits planar and highly polar side groups with high glass transition temperature ($T_g$) due to the presence of the rigid pyrrolidone group [82, 103]. The nature of the rigid pyrrolidone ring groups has been allowed higher ionic moment as compared to other semi-crystalline polymers like PVA. The mechanical strength and thermal stability of PVP can be improved because of the formation of the cross linked chain molecules [82, 168]. In addition, PVP have special attention among the conjugated polymers because of its good stability, highly soluble in water, and reasonable electrical conductivity.

In this connection, PVP mixed with PVA to increase in amorphous nature. The two blend polymers PVA and PVP electrolyte have functional group of hydroxyl (OH) and carbonyl (C=O) groups present in side chain which direct to the increase in conductivity. Moreover, it has unpaired electrons present in the side chain of PVA and PVP blending polymer, which leads to formation of complex further addition of amino acid [169]. The organic based amino acid materials play an important role in zwitterion formation. It has unique dipoles field like proton donor carbonyl group (COOH) and proton acceptor (NH$_2$) group. The proton H$^+$ ion donated by carboxylic group which attained negative charge (COO$^-$) like that the H$^+$ ion gained by amine group to form NH$_3^+$.

In general, amino acids have a Zwitterionic behaviour and they hold a deprotonated carboxylic acid group (COOH) and protonated amino group (NH$_2$) which helps in the enhancement of proton movement in blend polymer and molecular engineering for the tailor made applications. Among other biological substances, asparagine is a very important amino acid because it plays a major role in the metabolic
control of some cell functions in nerve and brain tissue and is also used by many plants as a nitrogen reserve source [170].

Recent research are reported that the amino acid speed up the rate of curing of injuries. Moreover, L-Asparagine helps to burning of excess of fats and it can be used in reducing weight [171]. This work deals with to prepare polymer membrane, 50% PVA: 50% PVP: 2.5% L-Asparagine which has the highest conductivity and characteristics of the membrane is studied with various analytical studies such as X-Ray Diffraction, FTIR spectroscopy and SEM. Further studies include Electrochemical Impedance Spectroscopy, which is used to find out the best optimum composition suitable for practical electrochemical application. The higher conductivity is found to be $1.5 \times 10^{-6}$ Scm$^{-1}$ for the composition of 50% PVA: 50% PVP: 2.5% L-asparagine at ambient temperature.

Literature survey illustrates that the ammonium based salts are good proton donors in to the polymer matrix [37, 149,172]. As reported in the literature, the proton conducting polymer electrolytes prepared using PVA as host polymer and CH$_3$COONH$_4$, NH$_4$SCN and NH$_4$X (X= Cl, Br, I, NO$_3$) as dopant salts [67, 68, 173, 174]. In addition, the studies of PVP doped ammonium halides like NH$_4$Cl [111] and NH$_4$Br [64] polymer electrolytes. The ammonium halides have decreasing order in lattice energy as NH$_4$Cl→NH$_4$Br→NH$_4$I to improvement of ionic conductivity. Hence, NH$_4$Br was chosen as the dopant since ammonium salts are considered as good proton donor [34, 169]. Here, the present work is designed to prepare the NH$_4$Br mixed PVA-PVP- L-asparagine blend polymer to enhance more ionic conductivity.

5.3 Experimental

5.3.1 Materials and Methods

Poly (vinyl alcohol) (PVA) with molecular weight of ~1,25,000 g and poly (vinyl pyrrolidone) (PVP) with molecular weight of ~90,000 g, were purchased from S. D. Fine Chemicals Ltd., and both the polymers were used without further purification. The salt L-Asparagine (Merck) and ammonium bromide- NH$_4$Br (Merck) are used as raw materials to synthesis the blend polymer electrolyte.
5.3.2 Polymer Electrolyte Synthesis

Biodegradable polymer electrolyte based on the composition of PVA, PVP, L-Asparagine and NH₄Br were blended by solution casting technique using double distilled water (D.D water) as solvent as shown in Figure 5.1. Stoichiometric quantities of precursor materials, PVA-50 m.wt.%, PVP-50 m.wt.% and L-Asparagine-2.5% m.wt.% are dissolved in D. D water separately and the above all solutions are continuously stirred for 1 hour at 40 °C to make the transparent solutions. The above PVP, PVA, L-Asparagine transparent solutions are mixed together with stirring until forming homogeneous blend solution. The NH₄Br salt with various concentrations (shown in Table 5.1) was dissolved in double-distilled water with vigorous stirring at room temperature. The resulting blended polymer was agitation for 24 hours for removing air bubbles or air gaps. The obtained homogeneous solution, PVA/PVP/L-Asparagine /NH₄Br blend was poured into polypropylene dishes and slowly dried at room temperature for 4 days. The obtained blend polymer film is detached from dishes for further studies. The coordination mechanism of PVA/PVP/L-Asparagine/doping NH₄Br is given in Scheme 5.1.

Table 5.1 Various compositions for PVA/PVP/L-Asparagine/doping NH₄Br polymer blend films

<table>
<thead>
<tr>
<th>Composition</th>
<th>PVA (m.wt.%)</th>
<th>PVP (m.wt.%)</th>
<th>L-Asparagine (m.wt.%)</th>
<th>Ammonium bromide (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>50</td>
<td>50</td>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>(b)</td>
<td>50</td>
<td>50</td>
<td>2.5</td>
<td>0.05</td>
</tr>
<tr>
<td>(c)</td>
<td>50</td>
<td>50</td>
<td>2.5</td>
<td>0.10</td>
</tr>
<tr>
<td>(d)</td>
<td>50</td>
<td>50</td>
<td>2.5</td>
<td>0.15</td>
</tr>
<tr>
<td>(e)</td>
<td>50</td>
<td>50</td>
<td>2.5</td>
<td>0.20</td>
</tr>
<tr>
<td>(f)</td>
<td>50</td>
<td>50</td>
<td>2.5</td>
<td>0.25</td>
</tr>
<tr>
<td>(g)</td>
<td>50</td>
<td>50</td>
<td>2.5</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Figure 5.1 Flow chart of synthetic route of solid state blend polymer electrolytes.
Scheme 1 Schematic representation of the coordination of proton ion in PVA/PVP/L-Asparagine/doping NH₄Br.

5.3.3 Characterization of the Polymer Films

X-ray diffraction pattern of the prepared polymer blend film have been recorded on a Bruker made X-ray diffract meter (D8 Advance ECO XRD Systems with SSD160 1D Detector) with Cu-Kα radiation in the Bragg angle 2θ range of 10° to 60° with the can rate of 2° per minute. FTIR spectra have been recorded for all the prepared polymer electrolyte films in the range of 400 to 4000 cm⁻¹ at room temperature using a SHIMADZU-side Fourier Transform Infra-red Spectrophotometer (IR Tracer-100). Impedance spectroscopy has been widely carried out to study the ionic conductivity of polymer thick films. The impedance study of the polymer electrolytes has been employed in the temperature range of 30 °C to 60 °C over a frequency range of 42 Hz to 1MHz using a computer-controlled HIOKI 3532 LCR analyzer. In this technique, the polymer films are cut in circular shaped and it is inserted in between two silver electrodes and the measurements were taken in every 10 °C interval from 30 °C to 60 °C. The conductivity
value calculated from the bulk impedance. Surface morphology and the microstructures
of PVA/PVP/L-Asparagine/NH₄Br polymer blend electrolyte films were examined using
Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometer (Carl Zeiss
EVO/18 with EDX spectrometer) at room temperature. Thermal properties (TGA/DSC)
were studied by a Perkin-Elmer (Model: DSC 4000) instrument and scanned at 10 °C/min
between 30 °C to 900 °C.

5.4 Results And Discussion

5.4.1 X-ray Diffraction Analysis

Figure 5.2 shows that the X-ray diffraction pattern of 50% PVA: 50% PVP blend: 2.5%
L-Asparagine: X gram (g) doped NH₄Br (X= 0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 g).

Figure 5.2 XRD pattern for different composition 50% PVA: 50% PVP: 2.5%
L-Asparagine: doping X g of NH₄Br (X= 0, 0.05, 0.10, 0.15, 0.20, 0.25 & 0.30 g).
The X-ray diffraction patterns show the curve implying the increase in the amorphous behaviour of different compositions of blend polymer films. PVA/PVP/L-Asparagine blend polymer electrolyte indicates amorphous nature which is identified uniform mixed polymer matrix as revealed in Figure 5.2(a-d). The amorphous broadness has varied at different glancing angle while adding NH$_4$Br mixed in PVA/PVP/L-Asparagine blend polymer. The amorphous manners are slightly modified and formation of crystalline peaks in which a maximum dissociation of salt of NH$_4$Br (> 0.15 g) with blend polymer matrix [150], as shown in Figure 5.2(e-g). These peaks are recognized as the recrystallization of NH$_4$Br on the film surface, which is identified from JCPDS data (PDF# 862947). On further addition of NH$_4$Br in blend polymer shows the increase in intensity of the NH$_4$Br peaks may be linked as unable accommodation of ammonium bromide in the blend polymer matrix. As a result, it improves the formation crystalline nature, which leads the reduction of the ion moment in free space and decrement of electrical conductivity [175].

5.4.2 Surface Morphology

Scanning electron microscopy (SEM) is clearly showed to illuminate the surface and the microstructure SEM morphology of PVA/PVP/L-Asparagine/NH$_4$Br polymer blend films electrolyte. The SEM micrographs of PVA/PVP/L-Asparagine blend and PVA/PVP/L-Asparagine/NH$_4$Br polymer blend films electrolyte are shown in Figure 5.12. For pure 50% PVA/50% PVP/2.5% L-Asparagine without NH$_4$Br salt blend film, a miscible and homogeneous polymer blend film was obtained by the mixing of PVA, PVP and L-Asparagine with NH$_4$Br, giving fine morphology till 0.15 g concentrations. For higher concentration of PVA/PVP/ L-Asparagine with NH$_4$Br blend film, polymer blend electrolyte films represent the crystalline nature and the dark polymer region indicates the amorphous matrix in the sample [140]. Thus, scanning electron microscopy conclusion is in agreed with the analysis XRD and FTIR studies.
Figure 5.12 SEM micrographs for different composition 50% PVA: 50% PVP: 2.5% L-Asparagine: doping X g of NH$_4$Br (X = 0, 0.05, 0.10, 0.15 & 0.20 g).
5.4.3 FTIR Analysis

The molecular interaction of prepared blend polymer films (50% PVA: 50% PVP: 2.5% L-Asparagine: NH₄Br) were studied from FTIR spectroscopy. Blending two polymers can provide more sites for ion hopping and exchange which lead to the increase in conductivity [37]. Figure 5.3 shows that the broad peaks are appeared in the region of 2800 to 3700 cm⁻¹ due to C-H, O-H and N-H stretching vibration of blended polymer (PVA, PVP) and L-asparagine. The broad peaks are observed in the pure blend PVA:PVP/2.5% L-Asparagine are 3352 cm⁻¹, 2922 cm⁻¹ and 1733 cm⁻¹ corresponds to N-H bonding, CH₂ asymmetric stretching, C-H stretching and also C=O stretching. The observed IR bands at 1639 cm⁻¹, 1287 cm⁻¹ and 842 cm⁻¹ are also attributed to C=C stretching C-O-C stretching and CH₂ bending respectively. FTIR bonds are obtained at 1428 cm⁻¹, 1100 cm⁻¹ and 742 cm⁻¹ due to C-H asymmetric deformation, CH₂ rocking and C-C skeletal vibration are observed respectively. The above FTIR bands Figure 5.3(a-d) are not changed up to 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.15 g NH₄Br and the bands are shifted when increasing towards higher concentration of NH₄Br in blend polymer as shown in Figure 5.3. Figure 5.3 show the shifted band 3010, 3016, 2800 cm⁻¹ from the region of 3352, 2922 cm⁻¹ owing to addition of NH₄Br up to 0.15 g in blend polymer [37] These are attributed to asymmetric stretching of NH₄⁺ mode and symmetric stretching of NH₄⁺ respectively which confirm that an interaction occurred between NH₄Br with blend polymer.

When increasing the concentration of NH₄Br in the blend polymer, NH₄⁺ ions have not merged with polymer. It signifies that the dissociation of surplus salt settled down as layer in the polymer matrix [37]. The carboxamide band formed at 1639 cm⁻¹ have slightly shifted to lower region and amine band at 1517 cm⁻¹ is disappeared for higher concentration. The broad FTIR band at 1428 cm⁻¹ is obtained due to C-H asymmetric deformation vibration and it has shifted to appearance of sharp peak. It may detachment of NH from L-Asparagine and it can be formed as NH₄ neutral ions at higher concentration of NH₄Br in blend polymer matrix.
Figure 5.3 FTIR pattern for different composition 50% PVA: 50% PVP: 2.5% L-Asparagine: doping X g of NH₄Br (X= 0, 0.05, 0.10, 0.15, 0.20, 0.25 & 0.30 g).

5.4.4 TG/DSC Analysis

TGA-DSC thermograms for the various compositions of PVA/PVP/L-Asparagine/mixed with NH₄Br are shown in Figure 5.4. From the plot, four different stages of the weight degradation and endothermic curves are observed for all the composition of blend polymers. Four stages of weight loss indicate nearly same thermal behaviour due to more thermal stability of polymer electrolytes. The first stage, endo thermic peak is observed the temperature range between 30 to 180 °C with the weight loss 10% indicate the removal of water molecules, acidic acid and some organic impurities etc. in the polymer. In the next stage, the endothermic curve in temperature range between 180 to 525 °C, with the weight loss 68%, the degradation of the weight of the polymer is obtained due to the decomposition of unstable organic residuals of PVA and PVP elements respectively. The heavy weight loss may conclude due to the partial breaking of organic
band and removal of filtrated organic compounds [176]. The endothermic peaks at third and fourth stages are obtained in the temperature range between 525 to 635 °C with weight losses 16% and % attribute to the removal of ammonium bromide molecule elimination of C-C molecules in the polymer electrolyte. In fourth stage, undoped PVA/PVP/L-Asparagine polymer has tiny endothermic peak than other composition, which indicated the association of ammonium bromide in the polymer. The endothermic peak is increased towards higher composition attributed to volatile residues formed by increment of salt in polymer.

Figure 5.4 TG/DSC thermogram of different composition 50% PVA: 50% PVP: 2.5% L-Asparagine: doping X g of NH₄Br (X = 0, 0.15, 0.30 g).
5.4.5 Electrical Impedance Studies

An impedance spectrum is used to analyze the microstructural behaviour of the materials. From the impedance analysis data, the graph between real ($Z'$) and imaginary ($Z''$) fragments of impedance for PVA/PVP/L-Asparagine/ NH$_4$Br polymer blend electrolyte films at different composition are shown in Figure 5.5. The obtained depressed semicircle with inclined spike specifies that the free moment of ions is formed in non-Debye nature. The depressed semicircle and inclined spike are obtained corresponds to series of capacitance connected with parallel combination of capacitor ($C_g$) and the bulk resistor ($R_b$) [177]. The bulk resistance is calculated from the end point of impedance at low-frequency semicircle which touch on the real axis ($Z'$) [109,110,140]. The bulk conductivity of polymer blend electrolytes of all compositions can be calculated from the bulk resistance ($R_b$) by using the following formula

$$\sigma = 1/R_b A$$ \hspace{1cm} \cdots (5.1)$$

Where, ‘$R_b$’ is bulk resistance, ‘$A$’ is cross sectional area and ‘$l$’ is the thickness of the polymer film. The highest conductivity is found to be $2.34 \times 10^{-4}$ Scm$^{-1}$ for the composition of 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.15g NH$_4$Br at ambient temperature (Table 5.2). The Cole-Cole plot of best ionic conducting composition 50% PVA: 50% PVP: 2.5% L-Asparagine/0.15 g NH$_4$Br with different temperature is shown in Figure 5.6. A typical Cole–Cole plot of all compositions of 50% PVA/50% PVP/2.5% L-Asparagine blend polymer doped with weight of NH$_4$Br films has been consisted an extended semicircular portion and reduction of inclined spike in the region of frequency at room temperature. From the Cole–Cole plots, it is known that diameter of the depressed semicircle decreases due to increase in temperature which implied that the bulk resistance ($R_b$) decreases. It is well known that the enhancement of conductivity at increasing temperature signifies the formation of voids available by amorphous area of the polymer blend electrolyte.
Figure 5.5 The cole–cole plot for different composition 50% PVA: 50% PVP: 2.5% L-Asparagine: doping $X$ g of $\text{NH}_4\text{Br}$ ($X= 0, 0.05, 0.10, 0.15, 0.20, 0.25 \& 0.30$ g) at ambient temperature.
Figure 5.6 The cole–cole plot for 50% PVA: 50% PVP: 2.5% L-Asparagine: doping 0.15 g of NH₄Br blend complexed with different temperature polymer blend electrolyte. The maximum conductivity of this particular composition polymer blend film has been found to be $4.95 \times 10^{-4}$ Scm⁻¹ at 60 °C. This result suggests that only the resistive component of the polymer electrolyte prevails when the temperature is increased. In Figure 5.7, it shows $1000/T$ vs log $\sigma T$ for 50% PVA: 50% PVP: 2.5% L-Asparagine with different weight of NH₄Br blend polymer electrolyte. It also shows the variation of ionic conductivity with respect to temperature for 50% PVA: 50% PVP: 2.5% L-Asparagine with different weight of NH₄Br blend polymer electrolyte. The linear variation of $1000/T$ vs log $\sigma T$ plots suggests a thermally activated conductivity can be equated as the Arrhenius law

$$\sigma T = \sigma_0 \exp(-E_a/KT)$$

... (5.2)

where, ‘$\sigma_0$’ is pre-exponential factor, ‘$T$’ means absolute temperature, ‘$E_a$’ means the activation energy and ‘$K’ is the Boltzmann constant. Arrhenius law is stated that the movement of the charge carrier from one transit site to another without having acquired
much energy. The activation energy for ion transport was calculated from the slope of the plot based on the above equation and it is significantly low for the blended polymer composition 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.15 g and 0.2 g NH$_4$Br possess highest conductivity as shown in Figure 5.8.

**Figure 5.7** Variation of conductivity with temperature different composition 50% PVA: 50% PVP: 2.5% L-Asparagine: doping X g of NH$_4$Br (X= 0, 0.05, 0.10, 0.15, 0.20, 0.25 & 0.30 g).
Figure 5.8 Conductivity and activation energy for the composition of 50% PVA: 50% PVP: 2.5% L-Asparagine: doping of NH₄Br.

Table 5.2 Conductivity for different concentrations of PVA, PVP and L-Asparagine doped with NH₄Br salt at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Ionic conductivity, $\sigma$ (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X= 0 g</td>
<td>X= 0.05 g</td>
</tr>
<tr>
<td>30 °C</td>
<td>2.63 x 10⁻⁶</td>
</tr>
<tr>
<td>40 °C</td>
<td>7.50 x 10⁻⁶</td>
</tr>
<tr>
<td>50 °C</td>
<td>3.30 x 10⁻⁵</td>
</tr>
<tr>
<td>60 °C</td>
<td>1.47 x 10⁻⁴</td>
</tr>
</tbody>
</table>

Table 5.3 Activation Energy ($E_a$) for various composition of polymer blends

<table>
<thead>
<tr>
<th>Activation Energy ($E_a$ in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% PVA: 50% PVP: 2.5% L-Asparagine with X g of NH₄Br salt</td>
</tr>
<tr>
<td>X= 0.05 g</td>
</tr>
<tr>
<td>1.1789 ± 0.041</td>
</tr>
</tbody>
</table>
The activation energy for 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.2 g NH₄Br is lower than other composition as shown in Table 5.3. Even though it has lower activation energy, the electrical conductivity is decreased than 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.15 g NH₄Br. It has showed crystalline peaks in XRD which indicate the dissociation of NH₄Br in the blend polymer. While increasing salt concentration in the blend polymer decrease the creation of voids which involve the decrement of ion movement in blend polymer. In the higher composition, the detachment of salt concentration in blend polymer point out the requirement of more activation energy to enhancement of conductivity.

5.4.6 Ionic Conductivity Studies

Figure 5.9 indicate the frequency dependent conductivity for all composition of different weight of NH₄Br mixed 50% PVA: 50% PVP: 2.5% L-Asparagine polymer films. It contains lower frequency plate region and higher frequency dispersion region. Polymer film at the composition 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.15 g NH₄Br has higher conductivity than others in which high range of pleatue region appeared. The Ac conductivities for 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.15 g NH₄Br are calculated for different temperature as shown in Figure 5.10. The lower frequency region is retained for all temperature and obtained dc conductivities are increased while increase in temperature. The activation energy is calculated from the temperature dependent dc conductivity plot using arrhenious behaviour [82]. The activation energy is found to be ~0.5 eV. It has showed higher activation energy compared with activation energy calculated by bulk conductivity.
Figure 5.9 Conductivity vs angular frequency for different composition 50% PVA: 50% PVP: 2.5% L-Asparagine: doping X g of NH₄Br (X= 0, 0.05, 0.10, 0.15, 0.20, 0.25 & 0.30 g).

Figure 5.10 Conductivity vs angular frequency for different temperature of 50% PVA: 50% PVP: 2.5% L-Asparagine: doped 1.5 g NH₄Br.
The excess energy may require breaking the bonds formed by H$^+$ of L-Asparagine and NH$_4$Br with polymer chain molecules and also for the ion movement. The formation of H$^+$ ion from the salt and amino acid is more helpful to enhance the dc conductivity for all the temperatures. The dielectric constant and dielectric loss are very high at lower frequency region. The charges are produced and immediately accumulated due to temperature and applied field at the electrode and electrolyte interfacial region. Hence, $\varepsilon'$ and $\varepsilon''$ values are increased at lower frequencies for various temperatures [64, 178]. Figure 5.11(i) shows the tan δ at various frequencies for all composition of different weight of NH$_4$Br mixed 50% PVA: 50% PVP: 2.5% L-Asparagine polymer films. M' and M" for various frequencies showed the obtained peaks at higher frequency which implies on increment of charge accumulation in electrode - electrolyte interfaces. The tanδ for different frequencies are also plotted for all composition of polymer electrolytes. The higher relaxation frequency appeared for 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.15 g NH$_4$Br polymer film. It realizes that the predominant dc conductivity obtained for long range hopping mechanism of ion charge carriers [107]. Figure 5.11(ii) represent the variation of frequency dependent tanδ for 50% PVA: 50% PVP: 2.5% L-Asparagine: doped 0.15 g NH$_4$Br, respectively. It has been noticed that tan δ is increased with increasing frequency, attain extreme value and immediately decreases towards the higher frequency. The tan δ peak heights are increased and sustain almost same relaxation frequency due to increasing temperature. The involvement of increasing peak height indicates that breaking of bond formation from the dipoles. The electrical conductivity obtained due to the production of charge carrier and mobility of the charge carriers. The protonic charges can be easily built by collision of ions in dipoles of the polymer chain molecules, which is identified from the increment of loss tangent peak height of blend polymer at increasing temperature. The slight increment of the relaxation frequency in loss tangent at increasing temperature indicates the long range mobility charge carriers in polymer chain molecules.
Figure 5.11 Variation of tan δ as function of frequency for (i) different composition 50% PVA: 50% PVP: 2.5% L-Asparagine: doping X g of NH₄Br (X= 0, 0.05, 0.10, 0.15, 0.20, 0.25 & 0.30 g) polymer electrolyte blend films. (ii) the composition 50% PVA: 50% PVP: 2.5% L-Asparagine: 0.15 g of NH₄Br.
5.5 Fabrication and Characterization of Solid State Battery

The greatest conducting polymer is applied as an electrolyte for battery applications [179]. The chemical reactions that possibly take place in the cell are

At the anode:

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e} \quad \ldots (5.3) \]

At the cathode

\[ \text{MnO}_3 + 6\text{H}^+ + 3\text{e}^- \rightarrow \text{Mn}^{3+} + 3\text{H}_2\text{O} \quad \ldots (5.4) \]

The parameters of solid state battery are specified in Table 5.4 and the voltage is measured for the synthesized polymer film (50% PVA: 50% PVP: 2.5% L-Asparagine). In this work, the cell \( \text{Zn}/\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} ||\text{polymer electrolyte}||\text{Mn}_2\text{O}_3 \) provide the voltage of \( E = 1.1 \text{ V} \). A steady state voltage of 1.1 V is obtained for the fabricated cell as shown in Figure 5.13 and it is constantly maintained till 81 hours. When the fabricated cell is discharging under the load applied 1 M\( \Omega \), the voltage of the fabricated cell remains stabilized at 0.8 V up to 54 hours. The variation of the theoretical and experimentally observed voltages is obtained due to the reaction of zinc at anode in the cell reaction. In the discharging state, voltage is slightly decreased and stabilized 0.8 V for 42 hours. After that the cell voltage is dropped continuously.

![Figure 5.13 Open circuit voltage (OCV) and discharge voltage as a function of time.](image)
Table 5.4 Cell parameters of fabricated solid state battery

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Cell parameters</th>
<th>Measurement value due to discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weight of the cell</td>
<td>1.5 g</td>
</tr>
<tr>
<td>2</td>
<td>Area of the fabricated cell</td>
<td>1.43 cm$^2$</td>
</tr>
<tr>
<td>3</td>
<td>Open circuit voltage</td>
<td>1.1 V</td>
</tr>
<tr>
<td>4</td>
<td>Discharge time for pleatue region</td>
<td>54 hr</td>
</tr>
<tr>
<td>5</td>
<td>Cell thickness</td>
<td>0.8 cm</td>
</tr>
</tbody>
</table>

5.6 Conclusions

NH$_4$Br mixed PVA/PVP/L-Asparagine blend polymer electrolyte films with various compositions have been prepared by solution casting technique. The FTIR and XRD analysis confirmed the amorphous nature and the complexion of PVA/PVP/L-Asparagine blend polymer electrolyte with NH$_4$Br salt. Higher concentration of NH$_4$Br was not dispersed in blend polymer which can confirm by crystalline behaviour and formation of NH$_4$ stretching bands. The Cole–Cole plots indicate that PVA/PVP/L-Asparagine blend can be effectively mixed with NH$_4$Br salt to enhance its conductivity. The increase in conductivity with increase in salt concentration can be attributed to the formation of charge carrier and charge transfer in blend matrix. The highest ionic conductivity of $2.34 \times 10^{-4}$ Scm$^{-1}$ with lower activation energy at room temperature has been observed for the composition of 50% PVA: 50% PVP: 2.5% L-Asparagine: doped 0.15 g NH$_4$Br polymer blend electrolytes film. The larger dc conductivity can be obtained due to creation of charge carriers in the polymer which is interpreted in dc conductivity and loss tangent results. Stolid state proton battery is fabricated and open circuit voltage is found to be 1.1 V.

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