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ECO – FRIENDLY PROTON BATTERY BASED ON PVA, PROLINE AND NH_4NO_3

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Abstract:

Eco-friendly proton-conducting solid polymer electrolytes were successfully developed using poly(vinyl alcohol) (PVA), proline, and ammonium nitrate (NH_4NO_3) through the solution casting technique. Polymer electrolyte membranes with different NH_4NO_3 concentrations (0.1–0.4 wt%) were prepared and characterized by using X-ray diffraction (XRD), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), AC impedance spectroscopy, transference number measurement and linear sweep voltammetry (LSV). XRD analysis revealed that the incorporation of NH_4NO_3 reduced the crystallinity of the PVA–proline matrix and enhanced its amorphous nature, while DSC results showed a significant decrease in the glass transition temperature, indicating improved polymer chain flexibility. FTIR spectra confirmed the complex formation and molecular interactions among PVA, Proline and NH_4NO_3. The polymer electrolyte containing 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% NH_4NO_3 exhibited the highest ionic conductivity of 7.76×10^{-4} S cm^{-1} at room-temperature with a low activation energy of 0.18 eV, demonstrating efficient proton transport. The electrolyte also exhibited a high ionic transference number ($t_{(ion)} = 0.9753$) and a wide electrochemical stability window of 3.23 V, confirming its suitability for electrochemical applications. A primary proton battery fabricated using the optimized polymer electrolyte delivered an open-circuit voltage of 1.73 V and maintained stable discharge characteristics. These findings demonstrate that the PVA–proline–NH_4NO_3 polymer electrolyte is a promising, biodegradable and environmentally friendly candidate for next-generation proton batteries and other solid-state electrochemical energy storage devices.

Keywords: Proton battery, Solid polymer electrolyte, Poly Vinyl Alcohol, Proline, Ammonium Nitrate, Ionic conductivity, Eco-friendly energy storage.

1. Introduction

In current years, accomplishment of proton conducting solid polymer electrolyte materials has inspired the researchers worldwide, owing to their applications in ionic devices such as batteries, fuel cell, gas sensors, smart window and super capacitors etc **[1 - 4]**. Poly (vinyl alcohol), poly (acrylonitrile), poly (vinyl pyrrolidone), poly (methyl methacrylate), and poly (ethylene oxide) are also used today (vinyl chloride) based host matrices have been used as solid polymer electrolytes in numerous electrochemical devices for their discrete advantages over liquid electrolytes such erosion less, effective mechanical properties, improved thermal stability, light weight, litheness and comfort of fabrication etc **[5]**. Among the several polymers, poly vinyl alcohol (PVA) is a semi crystalline polymer and getting a great engrossment since of its multitudinous avails such as awesome film making nature, high ductile strength, flexibility, biodegradability, non – toxic, biocompatibility, ease of processability, water solubility, high water permeability, Electrical and optical properties that are based on the dopant, low cost, chemical and thermal durability, and so on **[6, 7]**.

In the last few years, researchers have been monitoring the addition of inert – oxide fillers in addition to salts and plasticizers to the polymer matrix in order to achieve novel polymer electrolyte systems **[8]**. Commonly, amino acids are the basic units of proteins. Amino acids are important for protein synthesis and have diversified functions in the body and it can be extracted from the plants. Amino acids comprise an amino group (proton acceptor group (- NH_2)) and a carboxylic group (proton donor group (- COO)) and it can be categorized into two types (essential & non – essential amino acid). Non-essential amino acids are synthesized by the body, so they are not needed in the diet. Necessary amino acids, on the other hand, are not synthesized by the body and must be consumed by the diet. Amino acids are used in study of NLO and bio medical applications **[10 - 13]**. Bhuvaneshwari et al added the amino acid proline with PVA and reported the maximum ionic conductivity value of **1.24×10^{-5} S/cm** for 75 Mwt% PVA: 25 Mwt% Proline polymer electrolyte **[9].** Since studies show that ammonium salts are strong proton donors, the salt NH_4NO_3 (good fertilizer) were chosen for this analysis.

The current research focuses on the development based on various NH_4NO_3 (good fertilizer) salt concentrations with 75 Mwt% PVA: 25 Mwt% Proline membranes and its XRD, DSC, FTIR, LSV, and AC- impedance analysis techniques were used to investigate the structural, thermal, vibrational, electrochemical stability, and electrical properties of polymer electrolytes. For proton battery construction and transfer number calculation, the high proton-conducting polymer membrane is used.

2. Experimental Section

2.1. Materials and methods

The raw materials used in this study were the polymer PVA (Sigma Aldrich), the amino acid proline (LOBA CHEMIE) and the salt NH_4NO_3. Under continuous magnetic stirring, 75 Mwt% PVA and 25 Mwt% Proline was dissolved in DI water. Different (Mwt %) of NH_4NO_3 (0.1, 0.2, 0.3, and 0.4 (Mwt %) were dissolved separately in DI water. The two solutions were then combined and mixed for several hours before a homogeneous solution was obtained. After that, the solution was cast in polypropylene petridishes and baked at 50°C to produce clear and versatile films. Different characterization techniques were used to classify these polymer electrolytes. The following are the various polymer electrolyte systems that have been prepared:

- *
- *: 0.1 NH_4NO_3
- *: 0.2 NH_4NO_3
- *: 0.3 NH_4NO_3
- *: 0.4 NH_4NO_3

*Note: * indicate 75 PVA: 25 Proline*

3. Results and discussion

3.1. XRD analysis

Figure 1 displays XRD patterns of 75 Mwt% PVA: 25 Mwt% Proline with various NH_4NO_3 polymer electrolyte concentrations.

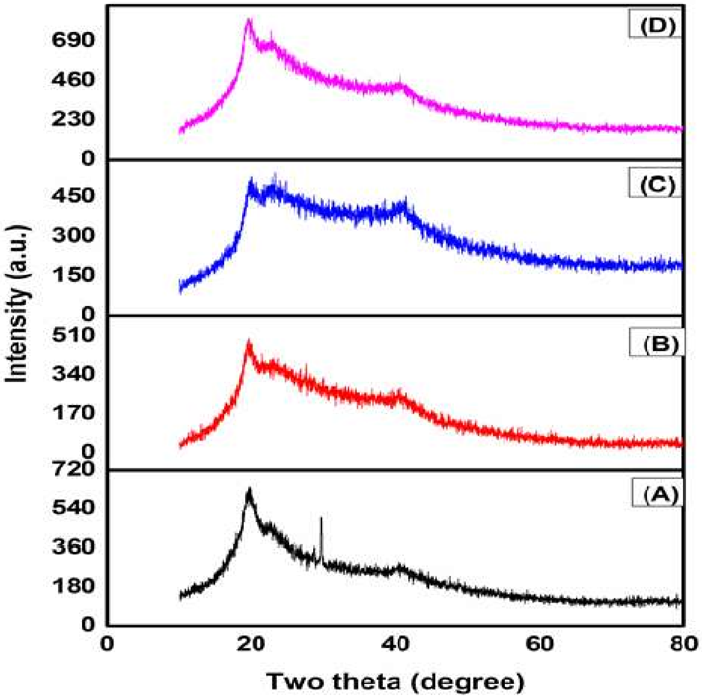


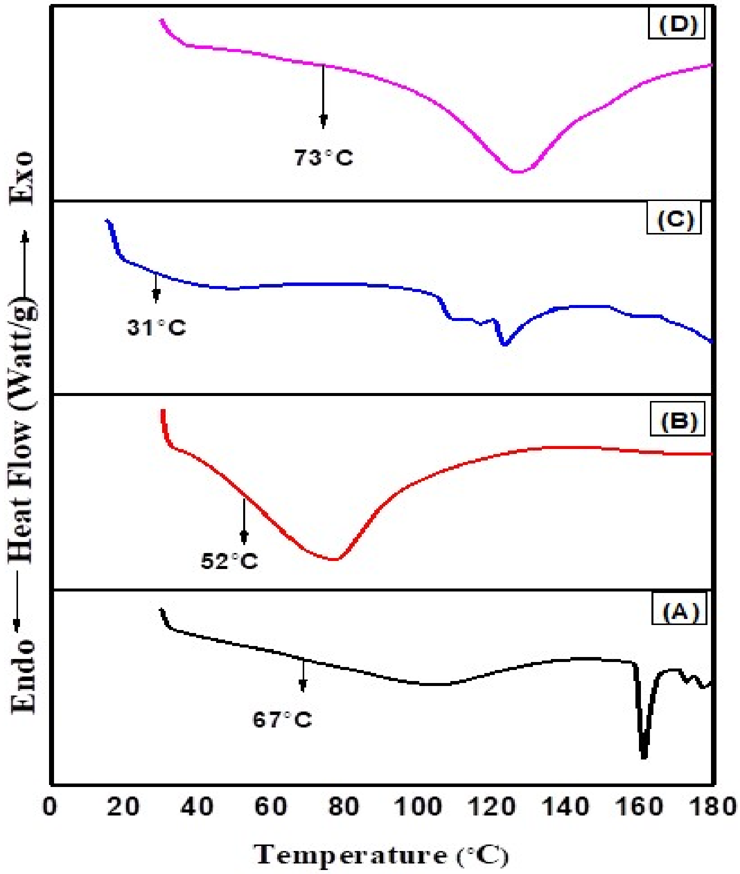
Fig.1: XRD patterns of (a) 75 PVA: 25 Proline (b) 75 PVA: 25 Proline: 0.2 (Mwt%) NH_4NO_3, (c) 75 PVA: 25 Proline: 0.3 (Mwt%) NH_4NO_3, 75 PVA: 25 Proline: 0.4 (Mwt%) NH_4NO_3 polymer electrolyte

In Fig. 1(A), the two diffraction peaks at θ = 19.64° and 40.2° are related to the semi-crystalline nature of pure PVA **[15, 16]**. With the addition of NH_4NO_3 salt concentrations up to 0.3 Mwt%, the width of these peaks increased marginally and their relative intensity decreased, suggesting a decrease in crystalline and an increase in amorphous of 75Mwt% PVA ratio 25Mwt % Proline. At a higher salt concentration of 0.4 Mwt % NH_4NO_3, the peak's width narrowed marginally while its relative intensity increased, indicating that the film's crystalline nature increased. No peaks are corresponding to NH_4NO_3 salt in prepared complexes, suggesting that the salt has completely dissociated in the polymer matrix **[17]**.

3.2. DSC Analysis

The prepared polymer electrolyte systems are further investigated to investigate the thermal characteristics using DSC as shown in Fig. 2.

Fig.2: DSC Thermograms of (a) 75 PVA: 25 Proline (b) 75 PVA: 25 Proline: 0.2 (Mwt%) NH_4NO_3, (c) 75 PVA: 25 Proline: 0.3 (Mwt%) NH_4NO_3, 75 PVA: 25 Proline: 0.4 (Mwt%) NH_4NO_3 polymer electrolyte



The glass transition temperature (T_g) decreases after the addition of salt NH_4NO_3 due to the plasticization effect of salt in the polymer PVA **[9]**, and proline structure (Fig. 2 (B, C)). Due to the presence of salts, the plasticizing effect is associated with the dipole-dipole interactions between the polymers chains are decreasing. The crystalline nature of the polymers PVA and Proline is disturbed by the addition of salt, resulting in weaker dipole-dipole. This clearly shows that a low T_g increases polymer light, allowing ions to easily pass through the polymer chain network in the presence of an electric field **[18]**. This low T_g leads to quicker the segmental motion, indicating that the amorphous phase is comparatively high, which is observed in the XRD studies. **Table 1** indicates the glass transition temperature of the various salt concentrations (NH_4NO_3).

Table 1 Glass transition temperature of PVA– Proline - NH_4NO_3 polymer electrolytes.

Composition of PVA/ Proline/ NH_4NO_3	**Glass transition temperature T_g (°C)**
75:25	**67**
75:25:0.2	**52**

75:25:0.3	**31**
75:25:0.4	**73**

3.3. FTIR Analysis

The formation of a complex between PVA, proline, and ammonium nitrate is revealed by FTIR analysis. Figure 3 depicts the FTIR spectra of all processed polymer electrolytes. From the table, the change

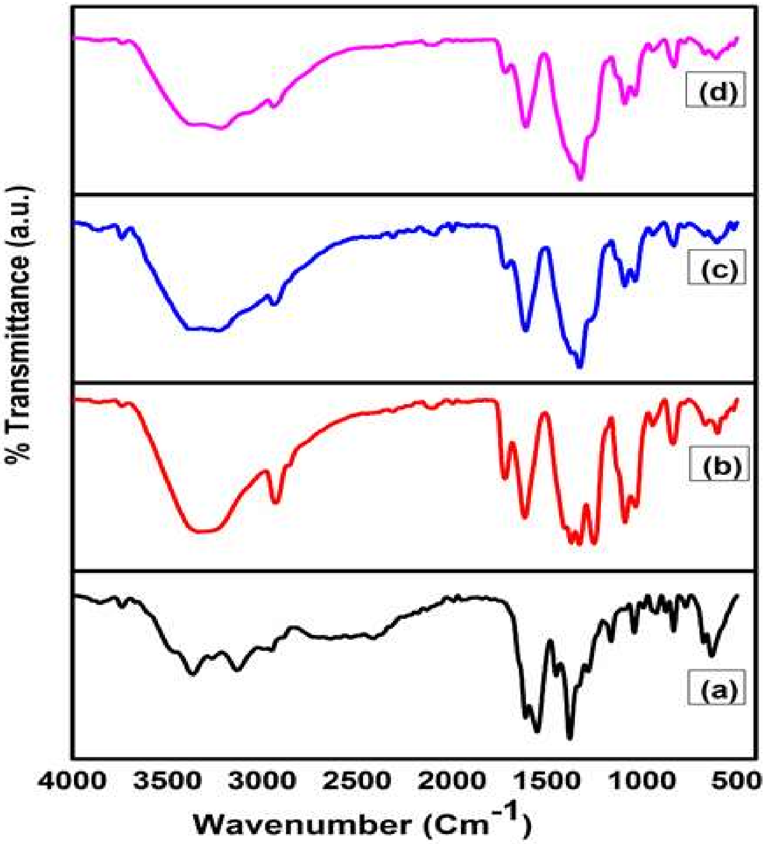


Fig.3: FTIR spectra of (a) 75 PVA: 25 Proline (b) 75 PVA: 25 Proline: 0.2 (Mwt%) NH_4NO_3, (c) 75 PVA: 25 Proline: 0.3 (Mwt%) NH_4NO_3, 75 PVA: 25 Proline: 0.4 (Mwt%) NH_4NO_3 polymer electrolyte

FTIR spectra clearly depict the interaction between the PVA: Proline: NH_4NO_3 polymer complexes.

The Vibrational peaks at 3373 cm^{-1}, 2961 cm^{-1}, 1602 cm^{-1}, 1369 cm^{-1}, 1036 cm^{-1} and 823 cm^{-1} assigned to O – H, C – H, C = C, CH_3, C = O stretching vibration and C – H rocking vibration of 75 Mwt% PVA: 25 Mwt% Proline is shifted in NH_4NO_3 added polymer electrolyte system respectively.

Table 2 The assignments of the peak position of all the prepared polymer electrolyte system.

Vibrational peaks of the polymer electrolytes (cm^{-1})	**Assignments**

75 PVA:25 Proline (Mwt%)	**75 PVA:25 Proline: 0.2 NH_4NO_3 (Mwt%)**	**75 PVA:25 Proline: 0.3 NH_4NO_3 (Mwt%)**	**75 PVA:25 Proline: 0.4 NH_4NO_3 (Mwt%)**	
3373	3339	3395	3395	O – H stretching
2961	2929	2929	2929	C – H (asymmetric stretching of CH_2)
1602	1613	1615	1602	C = C stretching
1369	1335	1337	1325	CH_3 symmetric stretching
1036	1090	1090	1090	C = O stretching
823	825	834	836	C - H rocking

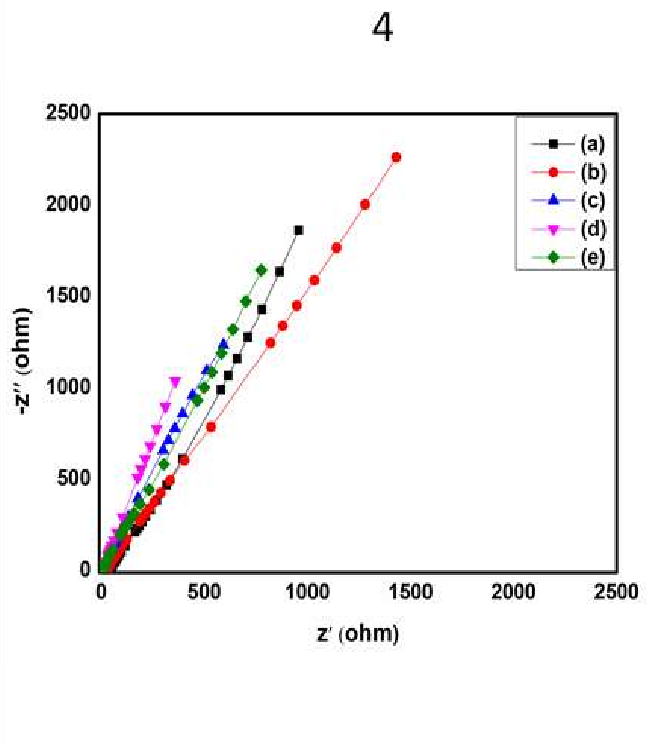
3.4. Impedance analysis

3.4.1. Cole-Cole plot

Cole – Cole plots of different concentrations of NH_4NO_3 added 75Mwt% PVA: 25Mwt% Proline polymer electrolytes is shown Fig. 4 at 303 K. The absence of the semicircle suggests that ion conduction is the primary cause of conductivity. The **(σ)** values of the polymer complexes were measured using the bulk resistance (R_b) obtained from the Cole – Cole map's intercept, the film area (A), and the film thickness (l).

$$\sigma = l/AR_b.$$

The calculated ionic conductivity and activation energy values are described in Table 3. Ionic conductivity rises with NH_4NO_3 and falls as NH_4NO_3 concentration rises. The concentration reaches the optimum amount (0.3 (Mwt%) NH_4NO_3), which gives the prepared polymer membranes the highest ionic conductivity. The dissociated ions of NH_4^+ and NO_3^- could combine to form ion pairs or ion bunches at higher salt concentrations, limiting the agility of charge carriers in the polymer matrix. Cole – Cole plots for 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% NH_4NO_3 is shown in Fig. 5 at various temperatures. The conductivity values increase corresponding to the increase of temperature. Because of the increased motion of charge carriers as the temperature rises, the ionic conductivity rises as well **[20]**.



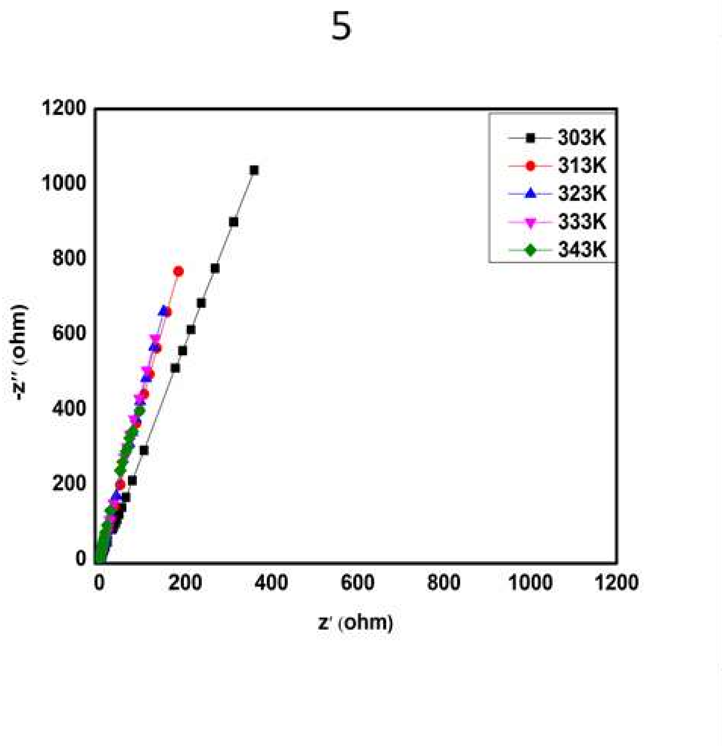


Fig.4: Cole – Cole plots for (a) 75 PVA: 25 Proline (b) 75 PVA: 25 Proline: 0.1 (Mwt%) NH_4NO_3, (c) 75 PVA: 25 Proline: 0.2 (Mwt%) NH_4NO_3, (c) 75 PVA: 25 Proline: 0.3 (Mwt%) NH_4NO_3, 75 PVA: 25 Proline: 0.4 (Mwt%) NH_4NO_3 polymer electrolyte at room temperature

Fig.5: Cole – Cole plot for 75 PVA: 25 Proline: 0.3 (Mwt%) NH_4NO_3 polymer electrolyte at various temperatures

Table 3 Ionic conductivity value of PVA: Proline: NH_4NO_3 polymer electrolytes at different temperatures.

Composition of PVA: Proline: NH_4NO_3 (Mwt%)	**Ionic conductivity σ_{dc} (S/cm)**				
	303K	**313K**	**323K**	**333K**	**343K**
75:25	7.66×10^{-5}	1.32×10^{-4}	1.7×10^{-4}	2.21×10^{-4}	2.58×10^{-4}
75:25: 0.1	1.35×10^{-4}	2.82×10^{-4}	3.54×10^{-4}	4.55×10^{-4}	5.05×10^{-4}

75:25: 0.2	5.89×10^{-4}	1.20×10^{-3}	1.74×10^{-3}	2.20×10^{-4}	2.61×10^{-3}
75:25: 0.3	**7.76×10^{-4}**	**1.56×10^{-3}**	**2.21×10^{-3}**	**2.61×10^{-3}**	**2.98×10^{-3}**
75:25: 0.4	3.39×10^{-4}	8.04×10^{-4}	1.29×10^{-3}	1.80×10^{-3}	2.40×10^{-3}

3.4.2. Temperature-dependent conductivity

The range of 303K to 343K Figure 6 shows. It has been discovered that as the temperature rises, the ionic conductivity rises as well. The increased free volume, as well as ionic and segmental agilities, is responsible for this. The Arrhenius relation can be used to calculate the activation energy for ion transport, E_a.

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

where σ_0 is the pre-exponential factor and E_a is the polymer electrolytes' activation energy. Our findings indicate that as the salt concentration rises, the activation energy value decreases until it reaches 0.3 (Mwt%) NH_4NO_3. This finding demonstrates that increasing the salt concentration increases both. If the salt concentration increases, the activation energy rises as well, owing to the accumulation of ions.

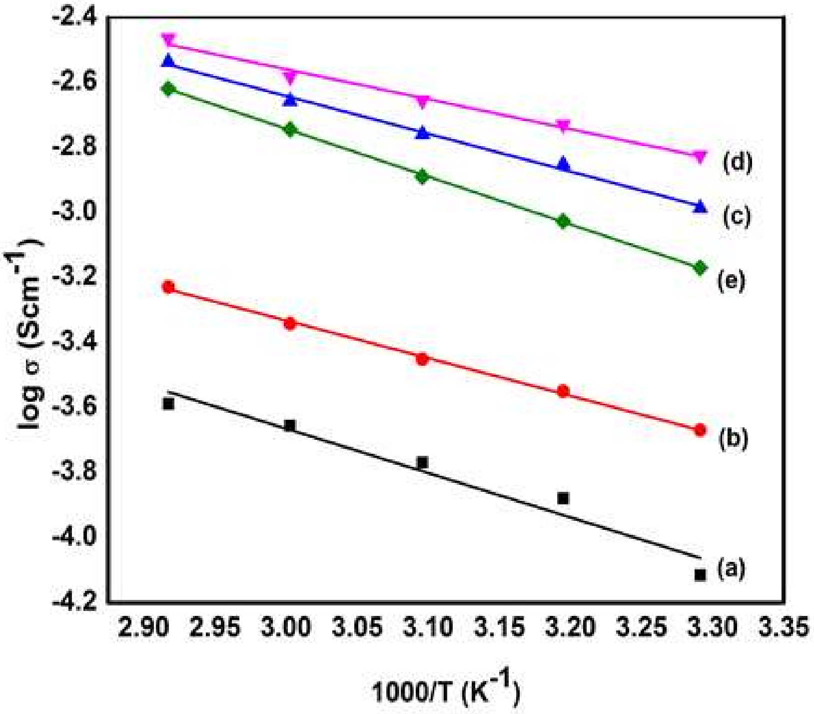


Fig.6: Arrhenius plot for (a) 75 PVA: 25 Proline (b) 75 PVA: 25 Proline: 0.1 (Mwt%) NH_4NO_3, (c) 75 PVA: 25 Proline: 0.2 (Mwt%) NH_4NO_3, (c) 75 PVA: 25 Proline: 0.3 (Mwt%) NH_4NO_3, 75 PVA: 25 Proline: 0.4 (Mwt%) NH_4NO_3 polymer electrolytes

Table 4 Activation energy and regression values for all prepared polymer electrolytes.

Composition of PVA: Proline: NH_4NO_3 (Mwt%)	**Activation energy (eV)**	**Regression values**
75:25	0.24	0.97
75:25: 0.1	0.23	0.99
75:25: 0.2	0.20	0.99
75:25: 0.3	**0.18**	**0.98**
75:25: 0.4	0.24	0.99

3.4.3. Concentration dependent conductivity

Figure 7 depicts the variance in room temperature conductivity (σ) and activation energy as a function of ammonium nitrate molecular weight percentage.

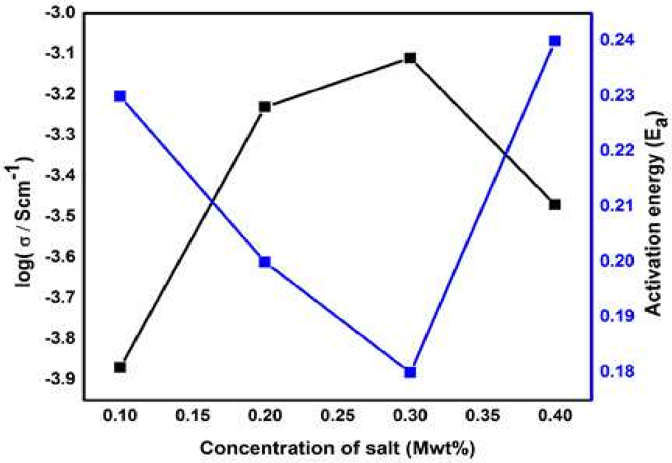


Fig.7: Variation of conductivity and activation energy of PVA: Proline: NH_4NO_3 as a function of salt concentration.

It was found that as the concentration of NH_4NO_3 rises up to 0.3 (Mwt%), the conductivity increases and E_a decrease. The energy barriers decrease as the number of analogous to the amorphous structure, accelerating ion transport. The rise of the PVA: Proline amorphous nature by NH_4NO_3, reduces energy constraints, allowing for faster ion transport.

3.5. Transference number measurement

The leading ionic conducting film's transference amount measured and Figure 8 shows its current versus time plot. The ionic transference number was calculated using the equation, tion, and the e-transference number, t_{ele}.

$$t_{ion} = (I_i - I_f)/I_i$$

$$t_{elec} = I_f / I_i$$

I_i is the initial current, and I_f is the final residual current as shown in Fig. 8 [21].

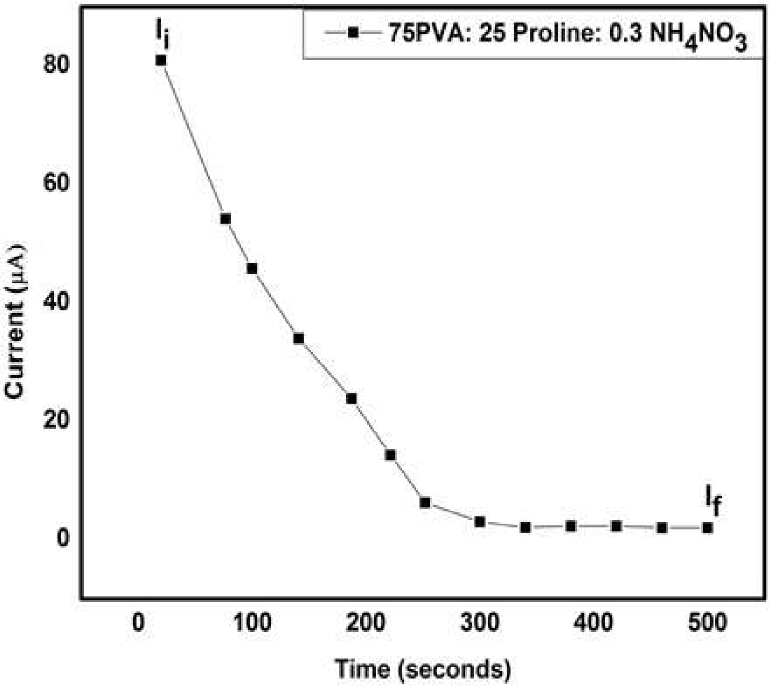


Fig.8: Variation of DC current as a function of time for the 75 PVA: 25 Proline: 0.3 (Mwt%) NH_4NO_3, polymer electrolyte

The largest conducting sample's ionic and e-transference numbers are $t_{ion} \sim 0.9753$ and $t_{ele} \sim 0.0246$, respectively. This result clearly showed that when H^+ ions from NH_4NO_3 interact with PVA: Proline becomes a near-perfect ionic conductor. Using the equations **[17]**, the cation and anion diffusion coefficients of 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% NH_4NO_3 is calculated.

$$D = D_+ + D_- = \frac{KT\sigma}{ne^2}$$

$$t_+ = \frac{D_+}{D_+ - D_-}$$

The ionic motion of cations and anions in all samples is calculated using the equations below.

$$\mu = \mu_+ + \mu_- = \frac{\sigma}{ne}$$

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-}$$

where e, k, T, n associated with the salt mixture, stoichiometric, and μ^+ and μ^- are the ionic mobility of cation and anion. The values of μ+ (1.21×10^{-6} $cm^2\ V^{-1}\ s^{-1}$) are higher than μ^- (3.1×10^{-8} $cm^2\ V^{-1}\ s^{-1}$) and D^+ (3.18×10^{-8} $cm^2\ s^{-1}$) are higher than D^- (8.6×10^{-10} $cm^2\ s^{-1}$) leading ionic conducting polymer electrolyte, indicating that the sample is cationic (+) rather than anionic (-).

3.6. Linear sweep voltammetry study

When using a polymer electrolyte in an electrochemical system, the electrochemical stability window is crucial. The leading ionic conducting polymer membrane was used to test electrochemical stability in a cell with two electrodes. The working electrode and the reference electrode are connected, with the working electrode acting as the working electrode and the reference electrode acting as the reference X-axis & Y-axis as a result. With a sandwich sample between two steel blocking electrodes, measurements were taken at a scan ratio of 0 - 5 V at 1 mV s1. I – V (Fig. 9(A) & 9 (B)) and P – V (Fig. 10(A) & 10(B)) curves of two different polymer membranes are clearly shows 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% NH_4NO_3 is advantageous to proton battery and electrochemical system applications **[20]**.

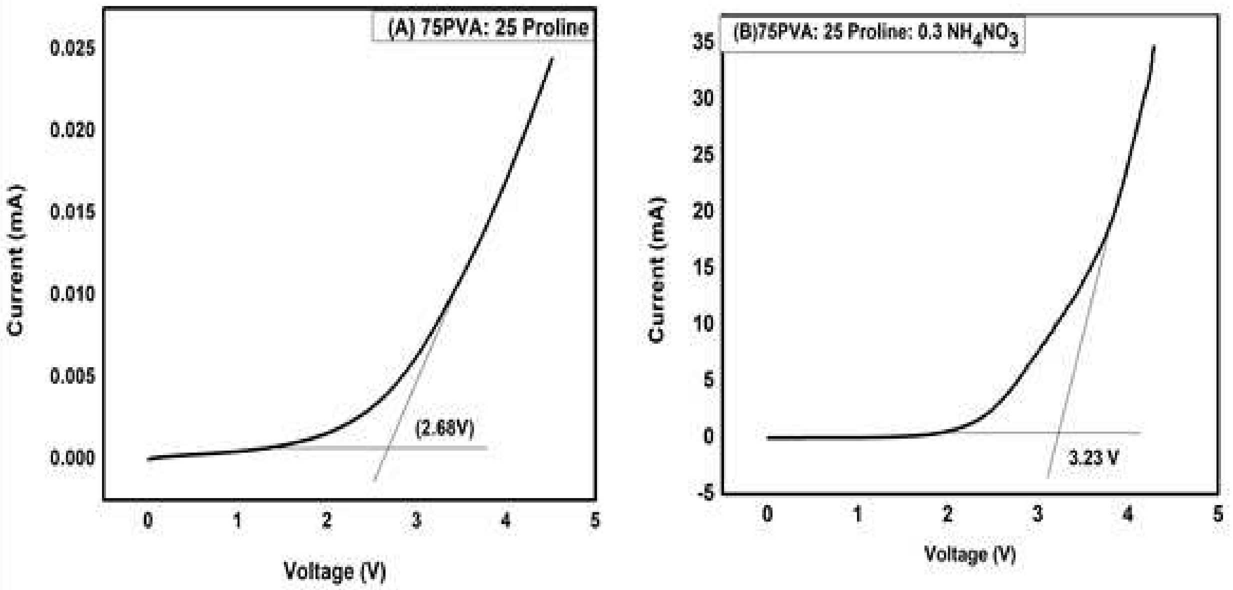


Fig.9(A) & 9(B): I – V Characteristics of (a) 75 Mwt% PVA: 25 Mwt% Proline and (b) 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% of NH_4NO_3 polymer electrolyte

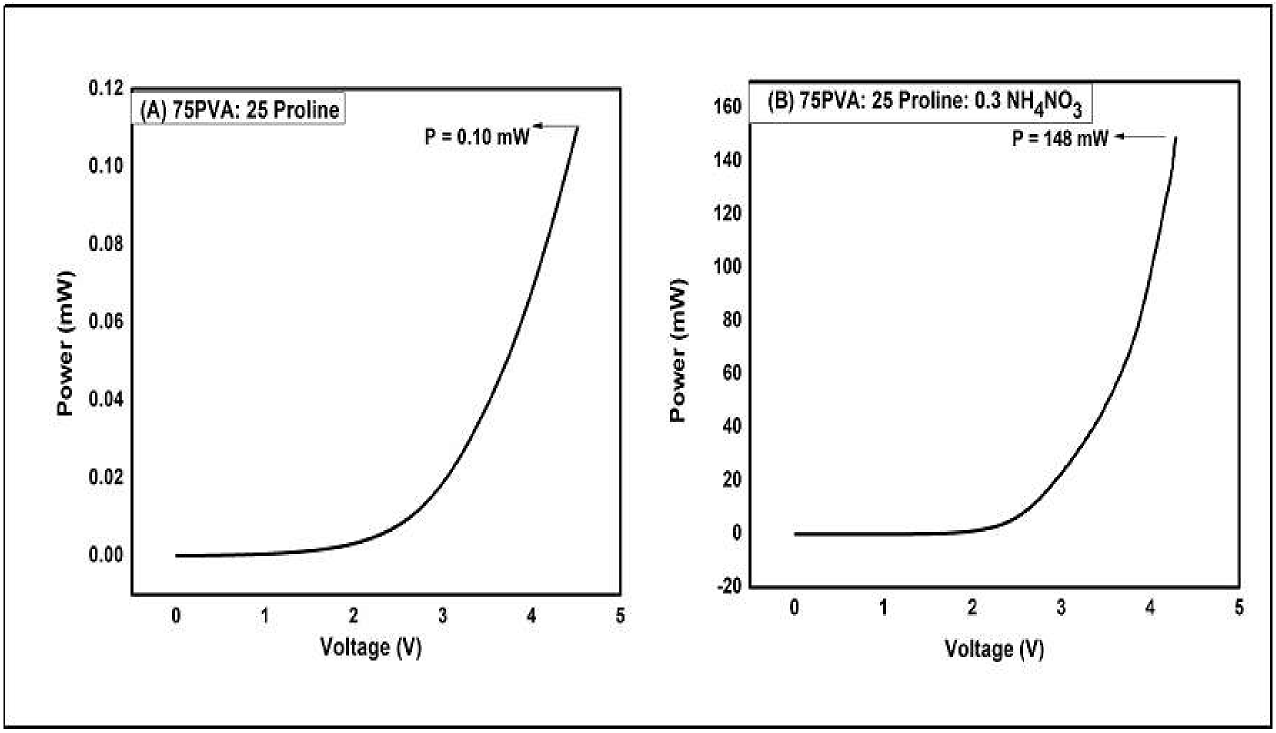


Fig.10(A) & 10(B) P – V Characteristics of (a) 75 Mwt% PVA: 25 Mwt% Proline and (b) 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% of NH_4NO_3 polymer electrolyte

3.7. Fabrication and characterization of primary proton battery

To build a proton battery, the highest conductivity polymer electrolyte (75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% NH_4NO_3) is combined with Zn + $ZnSO_4.7H_2O$ /75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% NH_4NO_3 / PbO_2 + V_2O_5. The appropriate amount of zinc (metal) powder (3 ratio), $ZnSO_4.7H_2O$ (1 ratio), and graphite powder (1 ratio) were mixed and pressed with a pressure of 5 tons to make a particle for the battery anode. Lead oxide (PbO_2) (8 ratio), vanadium pentoxide (V_2O_5) (2 ratio), graphite (1 ratio) and 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% NH_4NO_3 polymer electrolyte (0.5 ratio) were used to produce the cathode. Between the anode and the cathode, the highest conductivity polymer electrolyte was inserted; this configuration is mounted in the test open circuit voltage (OCV).

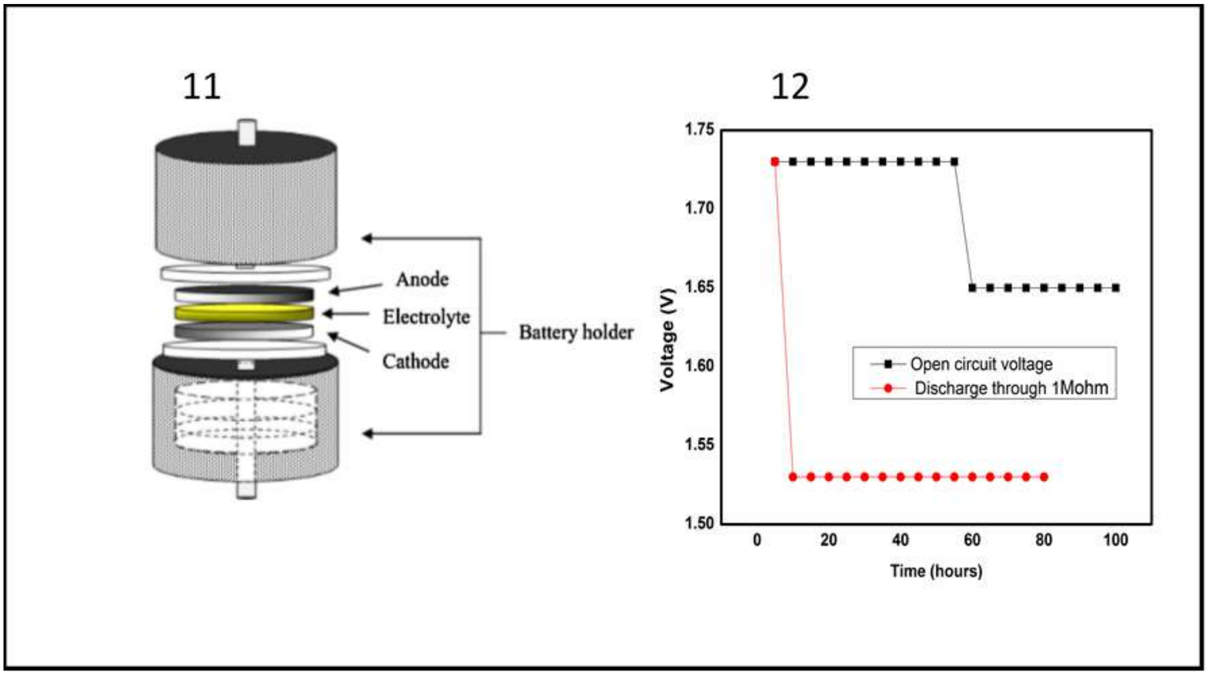


Fig.11: Schematic diagram of the battery configuration & Fig.12: Open circuit voltage and discharge curve of 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% of NH_4NO_3 polymer electrolyte

The anode and cathode reactions are given below:

Anode reaction

$nZn + ZnSO_4.7H_2O \rightleftarrows Zn_{n+1}(SO_4) . (7 - 2n) H_2O.2n(OH) + 2nH^+ + 2ne^-$

Cathode reaction

$PbO_2 + 4H^+ + 2e^- \rightleftarrows Pb^{2+} + 2H_2O$

$V_2O_5 + 6H^+ + 2e^- \rightleftarrows 2VO^2 + 3H_2O$

Figure 11, the OCV proton battery at room temperature. The tested cell's estimated OCV is 1.73V. This value decreases to 1.65 voltage assembled within the first 60 hours. Because of the polarization, the initial voltage drops between. The OCV was stable at 1.65 V for 40 hours after the cell voltage was normalized. 1.5 voltage (OCV) rated at 50 CA: 50 NH_4NO_3 biopolymer electrolyte **[22]**. The voltage is decreased to 1.53 V after the load is applied and remains constant for 70 hours. The polarization starting voltage decreases. Cell thickness is 0.267 cm, cell weight is 1.29 g, and OCV is 1.73 V. These are the most important cell parameters.

4. Conclusions

- XRD, AC impedance, FTIR, and DSC analysis techniques are used to characterize PVA- Proline - NH_4NO_3 based proton conducting polymer electrolytes.
- According to the XRD results, adding ammonium nitrate to the polymer matrix enhances amorphousness. The addition of NH_4NO_3 lowers glass transition temperature of PVA: Proline complexes.
- Vibration analysis shows the complex formation of polymer electrolytes (PVA/ Proline/ NH_4NO_3).
- At 303K, the highest ionic conductivity of 75 Mwt% PVA: 25 Mwt% Proline: 0.3 Mwt% NH_4NO_3 was estimated to be 7.76×10^{-4} S/cm.

- The prepared polymer electrolyte's temperature-dependent ionic conductivity follows Arrhenius' relationship and the maximum ionic conducting polymer membrane has low activation energy (0.18 eV).
- The highest conducting polymer membranes electrochemical stability window is 3.23 V.
- The transference number indicates that ions play a important role in charge transport in these membranes.
- The primary proton battery has been made and its specifications have been documented.

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