



# Synthesis and Studies on Polymer Electrolyte Membrane using Polyvinyl Alcohol, Polyvinylidene Fluoride and Ammonium Bromide as Dopants for Proton-conducting Electrolyte

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## ABSTRACT

Different compositions of Polyvinyl alcohol (PVA), Polyvinylidene fluoride (PVDF) and Ammonium bromide ( $\text{NH}_4\text{Br}$ ) were employed to synthesize the proton-conducting polymer electrolyte membranes by Solution casting method, which have potential applications in proton ( $\text{H}^+$ ) ion batteries and fuel cells. Structural, vibrational and electrical properties of the synthesized polymer electrolyte membrane were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy and Electrical Impedance Spectroscopy (EIS) analysis and results were reported. The semi-crystalline nature of the prepared polymer was confirmed by XRD analysis. FTIR spectroscopy revealed the vibrational spectra of the prepared polymer membrane. The Nyquist plot drawn from the AC Impedance analysis was a straight line, confirming the dielectric nature of the prepared membrane.

**Keywords:** Fuel cell; Polymer electrolyte; Proton-conducting; PVA; PVDF.

## 1. INTRODUCTION

Polymer electrolyte membrane (PEM) is fast becoming one of the best electrolytes for electrochemical energy storage devices and in the practical usage and importance in developing solid-state batteries, fuel cells and electrochromic devices (Hema *et al.* 2008). The main challenge in using polymer electrolyte membranes is to attain good ionic conductivity at ambient temperature.

A detailed literature survey suggested that Polyvinyl alcohol (PVA) is the main polymer used for the preparation of PEM by most of the researchers because it can conduct ions between the electrodes in a fuel cell (Gabriele *et al.* 2020). Since the ionic conductivity of the PVA membranes is not remarkable, the researchers are focused primarily on the enhancement of proton conduction between the electrodes of a fuel cell. The methods involve blending the polymer with another polymer and incorporating proton-conducting salts (doping).

Research articles (Rajendran *et al.* 2004) suggest that the polymer PVA is miscible with polyvinylidene fluoride (PVDF) with high intermolecular interaction. PVA is a polymer with carbon attached to a hydroxyl (-OH) group. The hydroxyl groups are involved in hydrogen bonding. Hence, it can be easily blended with other polymers (Li *et al.* 2010; Paul and

Barlow, 1980; Mijovic *et al.* 1997; Muthiah *et al.* 2013). PVDF is a semi-crystalline fluoropolymer with low surface energy, high permittivity, relatively low dissociation factor and high dielectric constant, which assists more ionization of salt, providing a high concentration of charge carriers. Ammonium salts, like Ammonium bromide ( $\text{NH}_4\text{Br}$ ), are good proton donors. The present work is focused on the synthesis and characterization of PVA-PVDF- $\text{NH}_4\text{Br}$  polymer electrolytes.

## 2. EXPERIMENTAL TECHNIQUE

PVA (Mw: 1,25,000, LR grade) as flakes, PVDF (Mw: 1,80,000, Sigma Aldrich, AR grade) as pellets,  $\text{NH}_4\text{Br}$  (LR grade) as powder salt and N, N-Dimethyl formamide (DMF) (extra pure 99% from Sisco Lab) were used as raw materials for the synthesis.

The polymer electrolyte membranes were prepared by the Solution casting technique with DMF as the solvent. The polymers PVA and PVDF were mixed in 80:20 ratios. Ammonium bromide was taken in three different amounts (2%, 4% and 6%) as the dopant. The hot plate was set at 200 °C and the raw materials PVA, PVDF and  $\text{NH}_4\text{Br}$  were brought together with DMF in a beaker and stirred with a glass rod manually until a homogeneous solution was obtained. The solution was then poured into a glass Petri dish to form a thin

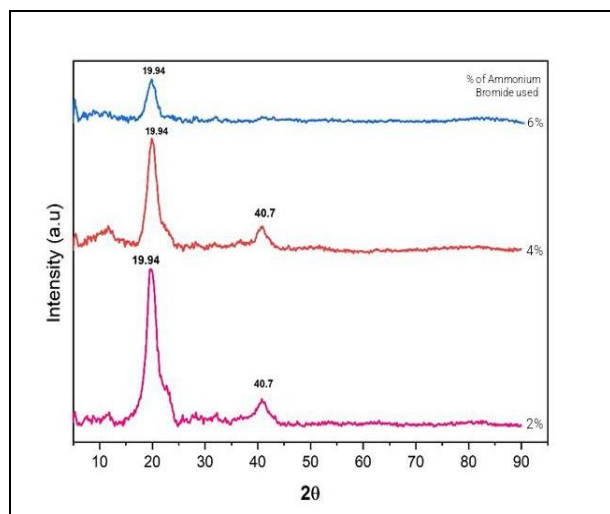
layer. The excess solvent that remained in the thin layer was removed by using the hot plate at 60 °C. The Petri dish was kept at room temperature for 24 h without any disturbance. The obtained blended polymer membrane was separated from the Petri dish for further studies.

The XRD (The third generation Empyrean, Malvern analytical multi-purpose diffractometer, Coimbatore, India) pattern was recorded using Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ). FTIR measurements were made (Schimadzu IR Affinity, Coimbatore, India) for studying the bonds in the prepared polymer blend membrane. The electrochemical impedance spectroscopy (EIS) of the membrane was done with an AC Impedance Analyzer from a frequency of 0.1 Hz to 10 kHz.

### 3. RESULTS AND DISCUSSION

#### 3.1 X-Ray Diffraction

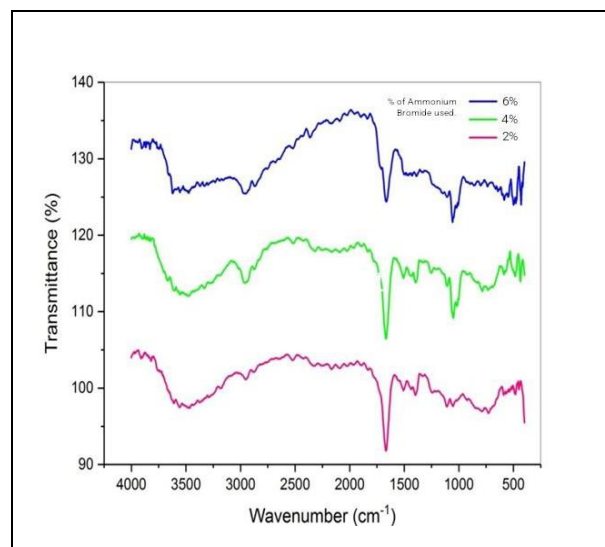
The structural properties of the produced polymer membrane were analyzed by X-Ray Diffraction method. From the obtained pattern, the properties such as semi-crystallinity and amorphous nature of the prepared polymer electrolyte membranes were inferred. The results were compared with that of the reference articles that characterized the pure PVA-PVDF membranes.



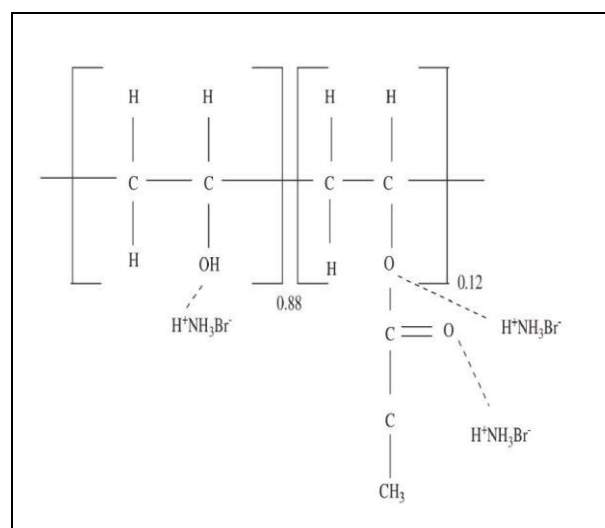
**Fig. 1: XRD graphs for various amounts of doping of NH<sub>4</sub>Br with PVA-PVDF blend**

The graphs for different amounts of NH<sub>4</sub>Br with the PVA-PVDF blend were obtained. An intense peak at 19.94° (2 $\theta$ ) in all three samples and a broad peak at 40° (2 $\theta$ ) in two of the samples were noticed. The results were compared with that of the reference articles that characterized the pure PVA-PVDF membranes and the peak values were matched (Pandey *et al.* 2011; Hema *et al.* 2008). Peaks corresponding to NH<sub>4</sub>Br (JCPDS file number 73–2355) were found to be absent in the complex systems, which indicates the complete dissociation of salt in the polymer matrix.

#### 3.2 FTIR Spectroscopy



**Fig. 2: FTIR results for various amounts of doping of NH<sub>4</sub>Br with PVA-PVDF blend**



**Fig. 3: Possible interaction of Ammonium bromide with the polymer**

FTIR spectra of 80:20 ratio mixed polymer blend PVA-PVDF with various concentrations of NH<sub>4</sub>Br (2, 4 and 6 wt. %) in the range 4000–400 cm<sup>-1</sup> were recorded.

From the literature survey, the vibrational peaks for pure PVA-PVDF polymer blend were observed at 431, 1094, 1726, 2925 and 3575 cm<sup>-1</sup> corresponding to CF stretching, CO stretching, C=O stretching, asymmetric stretching of CH and CH<sub>2</sub> and OH stretching respectively. The above-mentioned peaks get shifted to 449–428 cm<sup>-1</sup>, 1109–1056 cm<sup>-1</sup>, 1666–1664 cm<sup>-1</sup>, 2956–2951 cm<sup>-1</sup> and 3473–3487 cm<sup>-1</sup> for different wt. % of NH<sub>4</sub>Br. The peak appearing in the range 1666–1664 cm<sup>-1</sup> pertained to C=O in the acetate group in PVA. The peak

appearing in the range 3473-3487  $\text{cm}^{-1}$  can be assigned to the predominant OH stretching of alcohols.

The peak appearing in the range 449-428  $\text{cm}^{-1}$  indicated the existence of the  $\beta$ -phase crystallinity of PVDF. The  $\beta$ -phase of the PVDF polymer was due to the temperature of the synthesis method over 120  $^{\circ}\text{C}$  (Hema *et al.* 2008; 2009; Muthuvinaiyagam and Gopinathan, 2015; Brza *et al.* 2021).

The polymer's interaction with the doping salt has been shown in Fig. 3. Proton conduction can take place either by a single proton or by a group of protons.

### 3.3 Impedance Analysis

The prepared polymer electrolyte membranes were analyzed with AC impedance spectroscopy to obtain the impedance data. A Nyquist plot was made between  $Z'$  and  $Z''$ . A straight line was obtained at nearly 45 $^{\circ}$  between the x and y axes, showing that the prepared polymer electrolyte membrane was a material with a dielectric nature.

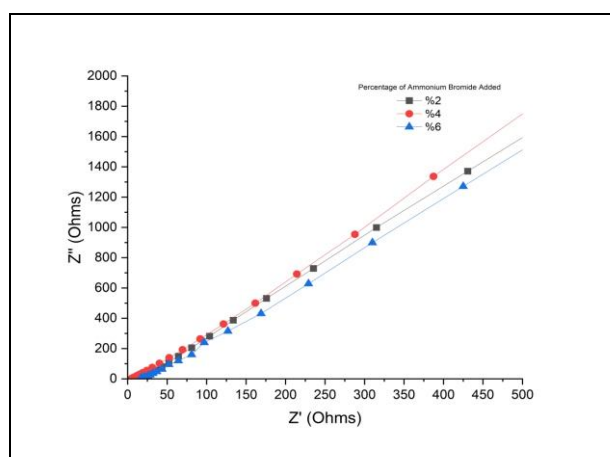


Fig. 4: Nyquist plot from Impedance analysis

### 4. CONCLUSION

The proton ( $\text{H}^+$ ) ion-conducting polymer membrane based on PVA, PVDF and  $\text{NH}_4\text{Br}$  was synthesised using Solution casting technique. Amorphous behaviour and vibrational assignments between polymers PVA, PVDF and  $\text{NH}_4\text{Br}$  have been confirmed by XRD and FTIR analyses. From AC impedance studies, the prepared membrane was found to be a perfect dielectric material. This results confirmed that these polymer electrolytes are well-suited materials for batteries, fuel cells, gas sensors and humidity sensors.

The PVA-PVDF blend polymers with various concentrations (> 6%) of  $\text{NH}_4\text{Br}$  were prepared and the suitable concentration of PVA-PVDF- $\text{NH}_4\text{Br}$  was selected according to the amorphous nature and ion

conductivity of the individual samples. Then the ion conductivity of the samples were analyzed at various temperatures and also the dielectric constant of the material was analyzed. The conclusions of the present studies highlight that choosing the appropriate polymer blend with a suitable amount of dopants can make the fabricated polymer electrolyte membranes suitable for electrochemical device applications.

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### CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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