

Electrical Impedance and Proton Conductivity Studies of Polymer Electrolyte Materials

K. Jeyabanu, P.Devendran, S. Asath Bahadur, N. Nallamuthu

Abstract: Solid electrolyte at different composition of 50% PVA + 50 % PVP + x% NaH_2PO_4 are prepared using solution casting techniques. The prepared materials of polymer matrices are characterized through several techniques such as XRD, FTIR spectroscopy. The electrical conductivity of the sample is determined through measured impedance data at different frequencies and different temperatures. The electrical conductivity is calculated in the order of 10^{-8} Scm^{-1} . The water uptakenability is also analysed. Proton conductivity is also analysed for various atmospheric condition.

Keywords— Solid electrolyte, PVA, PVP, protonic conductivity, Impedance

I. INTRODUCTION

Access to energy is key pillar and necessity in habitual life for poverty mitigation, human well being and economic development. However, our present available conventional energy systems have important environmental impacts. Historical and current energy systems are dominated by fossil fuels (coal, oil and gas) which produce carbon dioxide (CO_2) and other greenhouse gases. If we are to meet avoid dangerous climate change, the world needs a significant transition to an environmental friendly energy sources. Among various environment friendly energy sources, solid state batteries (SSBs) have become one of the best energy sources with negligible pollutant.

For fabricating solid state batteries, solid electrolyte are much intensively analysed due to its more qualities than liquid electrolytes. The following rectification is essential to lead solid state batteries like time consuming in charge and discharge behavior, resulting in leakage and reaction with electrodes. Solid state batteries have high potential to make it as miniature with high energy density. Applications of SSBs include high energy-density storage/conversion devices such as lithium ion batteries, super capacitors, fuel cell, etc.[1].

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Solid-state battery technology is not only used for faster recharging for electric vehicles and consumer electronics but also grid energy storage, medical devices and avionics.[2].

Recent work on rechargeable, all-solid-state alkali-metal batteries has advanced the technology to a point where applications through the whole battery product range can be envisaged. Amongst the accessible battery chemistries, proton conducting rechargeable batteries have now captured much attention due to its environmentally friendly nature, non-toxic and moreover low cost and abundant materials and thus can be used in large or medium scale industries.[3].

In development of solid state batteries, the electrolyte has much important role by the reaction between the electrodes during the charge and discharge process occurring in solid state batteries.[4]. The superionic conductors are synthesized in different forms such as glass, polymer, crystalline and composites. Solid polymer electrolyte has more advantages and has more participation effect in miniaturization of devices. Due to its advantages like easy to prepare, light weight, flexible in shape and size, good mechanical strength. High energy density and good electrode and electrolyte contact solid electrolyte selected polycrystalline materials for several manufacturing devices.[5].

Poly vinyl alcohol (PVA) is a semicrystalline polymer studied extensively because of its many interesting physical properties which arise from the hydrogen bond formation due to the presence of $-\text{OH}$ groups.[6-10]. Poly vinyl pyrrolidone (PVP) is a biopolymer with higher order of amorphosity, deserves a special attention among the conjugated polymers because of its good environmental stability, easy processability and moderate electrical conductivity.[11-14] The semicrystalline nature of PVA at room temperature, subsequently limits its ionic conductivity. One of the alternate way to enhance the amorphous nature of PVA based electrolyte systems is to blend with amorphous PVP polymer. The interactions between PVA and PVP is expected to occur through interhydrogen bonding between the carbonyl ($\text{C}=\text{O}$) group of PVP and the hydroxyl ($-\text{OH}$) group of PVA.[15-19].

In the present study, PVA and PVP blended polymer doped with different concentrations of sodium dihydrogen Phosphate have been prepared by the solution casting method, and the polymer electrolytes have been subjected into composition and conductivity analysis.

II. EXPERIMENTAL

A. Sample preparation

Stoichiometric amount of polyvinylalcohol and polyvinyl pyrrolidone are dissolved by distilled water individually. Sodium hypo phosphate is also made as aqueous solution. Both polymer precursor solutions are mixed with continuous stirring to obtain transparent solution. Thus, Sodium hypo phosphate solution is also mixed with the previous transparent solution. The final solution is stirred constantly with maintain temperature 60 oC. The sol is become gel after dried it in oven. The dried film formed from gel was characterised by several methods.

III. RESULTS AND DISCUSSION

A. X-ray diffraction (XRD) analysis

The structural characteristics of pure 50PVA/50PVP blends with different xwt% of NaPO₂H₂ [x= 1, 2, 3, 4 and 5%] were evaluated using X-ray diffraction studies and were shown in Fig. 1. There is no such well defined peaks were observed for pure PVP, instead a broad hump was observed at the region of 2θ = 10°-20°, which can be associated with the amorphous nature of pure PVA-PVP. While adding the salt in the blend polymer, four different humps are obtained. The relative intensity of the broad hump decreases by increasing the concentration of NaPO₂H₂. The intensity of broad hump in XRD pattern is low for PVA+PVP + 3% of NaPO₂H₂. XRD peaks corresponding to NaPO₂H₂ arenot found to be present in the Polymer blend electrolytes which indicate the complete dissolution of the salt in the polymer blend upto the concentration of 5wt% of NaPO₂H₂. The amorphous nature results in high ionic conductivity of the polymer blend electrolyte.[20].

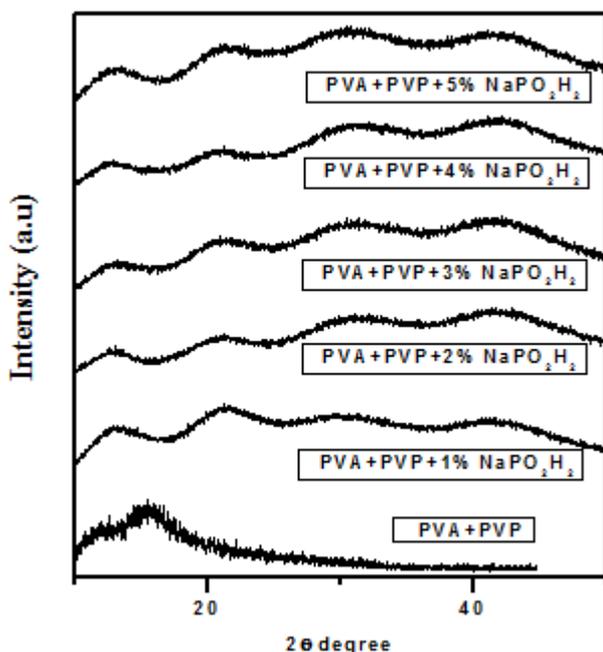


Fig.1. XRD pattern for NaPO₂H₂ mixed PVA+ PVP polymer sample.

B. Water uptake measurement

protonic conductivity performance of the materials are enhanced depends on the existing water molecule and water uptaken in the sample. The mechanical properties of the polymer film is also obtained due to water up taken capability of the sample. Water uptake measurement or gravimetric technique are performed to determine the swelling properties of the polymer where the 50PVA/50PVP doped with x wt% of NaPO₂H₂ blends were immersed in water at room temperature. The following formula is determined

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} * 100\%$$

where w_{dry} is the mass of the dried sample before the measurement and w_{wet} the mass of the wet sample.

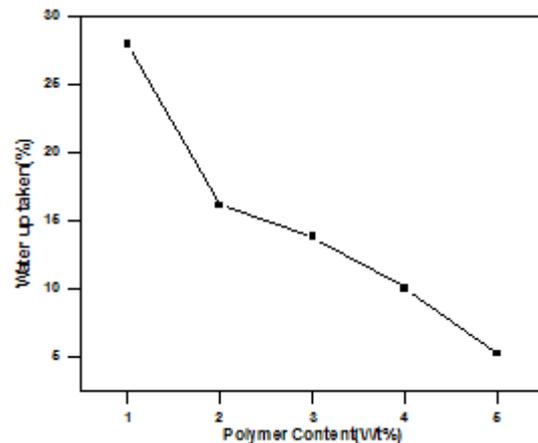


Fig.2. Water uptake measurement for various composition of blend polymer films.

Fig. 2. is displayed the water uptaken values for all the composition of PVA-PVP mixed sodium hypo phosphate samples. 1% NaH₂PO₂ is having more water uptaken values and it is decreased for increasing salt concentration in polymer matrices [21].

C. Ion Exchange capacity

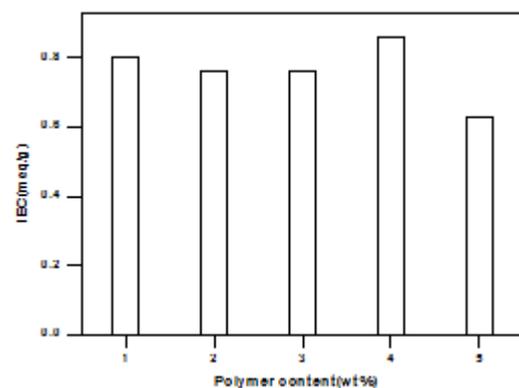


Fig.3. Ion exchange capacity for NaPO₂H₂ mixed PVA+ PVP polymer sample.

Ion exchange capacity is measured by back titration. At first, sample is washed by distilled water to remove any impurities observed on the surface of polymer film. The resulted polymer is immersed in 0.01M HCl and then it titrated by NaOH solution. Here Phenolphthalein is used as indicator [22]. The Ion



membrane capacity is slightly high for 4% Sodium Hypo Phosphate +PVA –PVP polymer matrices.

D. Protonic Conductivity

Protonic conductivity is calculated from measured impedance of sample at different frequencies at different atmosphere. The sample of 1% provide higher protonic conductivity for 100%RH. While increasing the concentration, the proton conductivity is decreased. At 4% polymer, it has also showed the better conductivity. At the lower composition, the protonic conductivity is obtained due to the existing OH molecules and obtained pore molecules. The proton movement is also increased with increasing ICE and water uptaken values. At higher composition, the conductivity is obtained due to the increasing water molecules in polymer films [23].

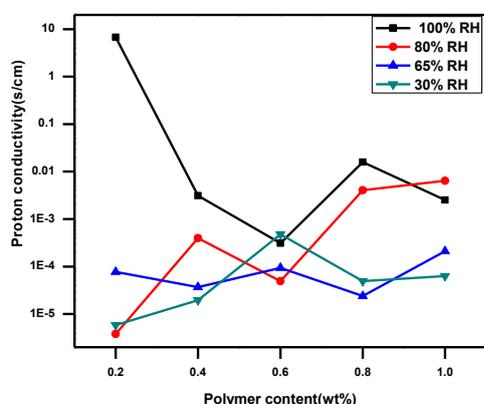


Fig. 4. Protonic conductivity of all the composition of polymer matrices

IV. CONCLUSION

PVA and PVP mixed sodium hypo phosphate at different compositions were prepared by solution-casting method. The prepared samples showed the amorphous nature for blend polymer and all the various composition of Sodium hypophosphate salt mixed blend polymer. The amorphous nature enhances the ionic conductivity for polymer sample. Protonic conductivity, water uptake measurement and Ion exchange capacity are also analysed for all the blend polymer sample. The protonic conductivity is higher for 4wt% of sodium hypo phosphate mixed sample than other all composition.

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