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Effect of Adipic acid on PVA based proton conducting polymer electrolyte

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Abstract
The proton conducting solid polymer electrolytes composed of Poly vinyl Alcohol (PVA) with different concentration of adipic acid ($C_6H_{10}O_4$) have been developed by using solution casting technique. The prepared polymer electrolytes have been subjected to XRD, DSC, AC impedance and Wanger's dc Polarization studies. XRD analysis confirms amorphous nature of polymer electrolytes. DSC analysis reveals that the best ion conducting sample 75 PVA: 25 $C_6H_{10}O_4$ polymer electrolyte has more thermal stability than pure PVA polymer electrolyte. The highest ionic conductivity has been found to be 7.50×10^{-5} Scm^{-1} at 303 K for 75 PVA: 25 $C_6H_{10}O_4$ polymer electrolyte. Temperature dependent conductivity of polymer electrolytes obeys Arrhenius equation. The highest conductivity polymer electrolyte 75 PVA: 25 $C_6H_{10}O_4$ has low Activation energy 0.2744eV among the prepared polymer electrolytes. The transference number of electrolyte in the highest ion conductivity sample is 0.95. Wanger's dc Polarization analysis suggests that the prepared polymer electrolytes are the best proton ion conductors.

Keywords: XRD, DSC, AC impedance, Wanger's dc Polarization

1. Introduction
In recent years there has been much interest in ion conducting polymers which show high ionic conductivity at room temperature because these are the most promising electrolytes in various electrochemical devices such as all solid-state batteries, sensors, fuel cells etc. Poly (vinyl alcohol) is semicrystalline polymer and cost effective biodegradable synthetic polymer with high tensile strength and flexibility. It contains hydroxyl group attached to methane carbons which acts as a hydrogen bonding source. Adipic acid ($C_6H_{10}O_4$) is a white crystalline powder. This organic compound is the most important synthetic dicarboxylic acid. It has a wide range of applications like coatings, plasticizers and detergents. Adipic acid is readily biodegradable and has a low potential for bioaccumulation.
The intention of the present work is to prepare and characterize polymer electrolytes based on PVA with different compositions of $C_6H_{10}O_4$. The prepared samples have been subjected to X-Ray Diffraction, Differential Scanning Calorimetry, Ac impedance Spectroscopy and Wagner's dc polarization technique.

2 Experimental Technique
2.1 Sample Preparation
PVA with average molecular weight 125,000 (AR grade, sd fine chem) and adipic acid ($C_6H_{10}O_4$) have been used as starting materials to prepare proton conducting polymer electrolytes. PVA based solid polymer electrolytes of various molar ratios of adipic acid such as (100:0), (80:20), (75:25), (70:30) have been prepared by the solution casting technique. Appropriate quantity of PVA and adipic acid are dissolved in the solvent dimethyl sulphoxide (DMSO) separately. Then these solutions are mixed together and stirred well to get homogeneous mixture. The resulting solution is poured on to glass petri dishes and is allowed to vacuum dried in the vacuum oven for 5 days at 70 ^0C, in order to remove the solvent. The smooth uniform flexible polymer films which are transparent to visible light have been obtained.

2.2 Characterization

2.2.1X – ray diffraction studies

XRD spectra have been recorded in Philips X'PERT – PRO diffractometer using CuKα radiation (λ=1.5406A^0) in the range of 2θ = 10^0–80^0 at a scan rate of 10^0/min to examine the crystallinity of the polymer electrolytes.

2.2.2 DSC studies

DSC thermo – grams have been obtained using Perkin – Elmer system DSC7 at heating rate of 5K/min under nitrogen atmosphere in the temperature range 260K–450K to investigate the glass transition temperature of the prepared polymer electrolytes.

2.2.3 Conductivity measurements

AC conductivity measurements have been carried out on PVA: Adipic acid systems of uniform thickness having an area of 1 cm^2. Polymer electrolytes have been sandwiched between two stainless steel (SS) electrodes applying a potential of 1V from 42 Hz to 1 MHz using HIOKI make LCZ meter (model 3532) interfaced to a computer. The conductivity has been calculated from complex impedance plots of measured impedance (Z) and phase angle (θ). The temperature of the cell has been controlled using a thermostat and electrical measurements of the polymer electrolytes have been carried out in the temperature range 303K–343K.

2.2.4 Wagner's DC Polarization technique

The Transference number has been made using Wagner's DC Polarization technique.

3. Results and Discussion

3.1 X-Ray Diffraction Analysis

Figure 1 shows XRD patterns of [P] Pure PVA, [Q] 80 PVA: 20 $C_6H_{10}O_4$, [R] 75 PVA: 25 $C_6H_{10}O_4$, [S] 70 PVA: 30 $C_6H_{10}O_4$ polymer electrolytes. The characteristic peak of pure PVA appears at 2θ =19.39°. This peak gets shifted in the adipic acid added samples at 2θ = 21.58°, 21.02° and 21.76° in 20mol%,25mol% and 30mol% adipic acid doped samples respectively. The other peaks present at 2θ = 25.38°, 31.03°, 32.70° and 38.55° may be due to incomplete dissociation of adipic acid in the polymer electrolyte. Besides it has been observed that 25mol% doped electrolyte has the highest intensity at the peak of 25.38° due to proton ion occurred in the present samples and accommodated to the values of the conductivity obtained (Rozali *et al.*, 2015) [1].

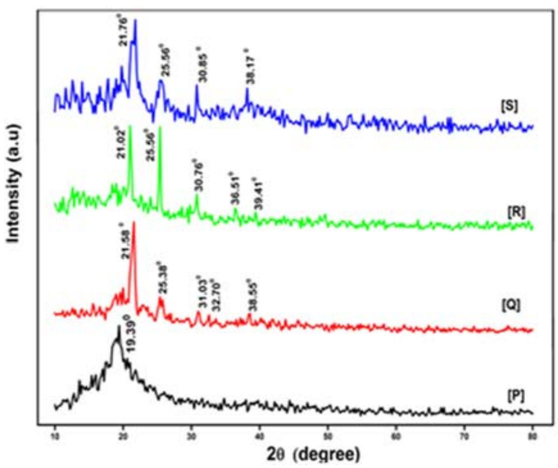

Fig 1: XRD patteren of [P] Pure PVA, [Q] 80 PVA: 20 $C_6H_{10}O_4$, [R] 75 PVA: 25 $C_6H_{10}O_4$, [S] 70 PVA: 30 $C_6H_{10}O_4$ polymer electrolytes.

3.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) technique provides information about thermal properties such as glass transition temperature (Tg), melting temperature (Tm) and crystallization (Tc) temperature of the polymer electrolyte. Figure 2 shows the DSC thermograms of Pure PVA, and (100 –X) PVA:X adipic acid (X=20, 25, 30 mol%) in the range of temperature from 0°C up to 250 °C. The melting point is a physical parameter used to identify the nature of the substance like stability and its degree of purity.

From the plot, it has been observed that the melting temperature of pure PVA electrolyte is 188.47 °C which is less than the reported value in the literature. Also it is noticed that 25mol% adipic acid doped polymer electrolyte has the highest melting temperature among the prepared electrolytes. It reveals that it has more stability than that of pure PVA electrolyte (Lawal Sa adu *et al.,* 2014) [2].

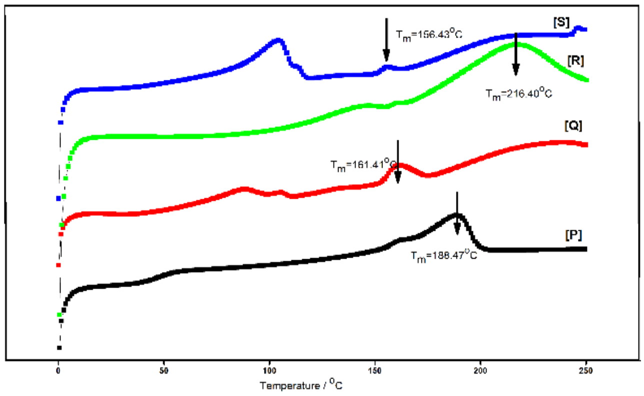

Fig 2: DSC spectra of [P] PURE PVA, [Q] 80 PVA: 20 $C_6H_{10}O_4$, [R] 75 PVA: 25 $C_6H_{10}O_4$, [S] 70 PVA: 30 $C_6H_{10}O_4$ polymer electrolytes.

3.3 Temperature Dependence of Ionic Conductivity

The temperature dependence of proton conductivity for all the prepared PVA: $C_6H_{10}O_4$ (mol %) polymer electrolytes over the temperature range 303K-343 K are shown in Figure 3. It is seen that the conductivity increases linearly with increase of temperature for all compositions of polymer electrolytes. When the temperature is increased, the ionic mobility of the polymer chain is enhanced and the fraction of free volume in a solid polymer electrolyte increases accordingly, which leads to an increase in the ionic conductivity of the polymer electrolyte. In addition, the number of charge carriers increases with temperature resulting in an increase in the ionic conductivity at higher temperatures.

The polymer electrolytes doped with 25 mol % $C_6H_{10}O_4$ exhibits the highest ionic conductivity 7.50 X 10^{-5} Scm^{-1} at 303 K among the prepared samples. Regression values of all electrolytes are close to unity (Table 1). It suggests that the polymer electrolytes obey Arrhenius equation, $\sigma = (\sigma_o/T) \exp(-E_a/kT)$

Where σ_o is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann constant

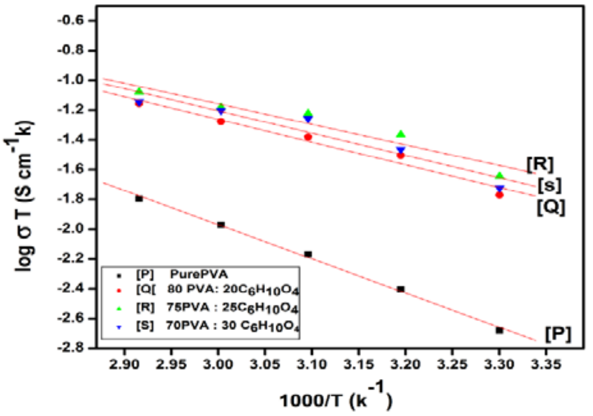

Fig 3: Temperature dependent ionic conductivity of PVA: $C_6H_{10}O_4$ Polymer electrolytes with different concentrations.

The activation energy for ion transport of all the prepared polymer electrolytes has been calculated by linear fit of the Arrhenius plot and are tabulated in Table 1. The activation energy decreases with increase in salt concentration upto 25 mol % adipic acid. At higher salt concentrations the activation energy increases due to aggregation of ions, leading to the formation of ion clusters, thus decreasing the number of mobile charge carriers (Sivadevi *et al.* 2013) [3]. The activation energy has been found to be low (0.2744 eV) for the best conducting polymer electrolyte.

Table 1: Activation energy value, Regression value, transference number of ions & electrons for different compositions of PVA: $C_6H_{10}O_4$ Polymer electrolytes

PVA : $C_6H_{10}O_4$ (mol %)	Activation Energy (eV)	Standard Value	Regression Value	t_{ion}	t_{ele}
100 : 0	0.4570	0.02308	0.99837	---	---
80 : 20	0.3029	0.04797	0.98435	0.94	0.05
75 : 25	0.2744	0.07155	0.95919	0.95	0.04
70 : 30	0.2972	0.07908	0.95762	0.93	0.06

3.4 Transport analysis

Total ionic transference number of polymer electrolytes has been measured using Wagner's Polarization technique (Wagner *et al.* 1957) [4]. This technique has been used to analyze the mobile species in the electrolyte is either ions or electrons. A fixed DC voltage is applied to the Wagner's polarization cell contains CP/(75PVA: 25$C_6H_{10}O_4$ polymer electrolyte)/ CP [CP – copper plate.

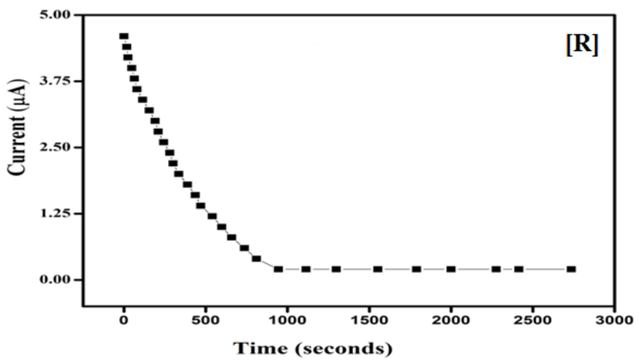

Fig 4: Time dependence of Wagner's dc polarization current of the cell with 75 PVA: 25 $C_6H_{10}O_4$ Polymer electrolyte. at 303K

The polarization current passing through the cells has been monitored as a function of time. Figure 4 shows polarization current vs. time plot of the best conducting electrolyte. Similar measurements have also been done for other samples Pure PVA, 80 PVA: 20 $C_6H_{10}O_4$, 75PVA: 25 $C_6H_{10}O_4$, 70PVA: 30 $C_6H_{10}O_4$ polymer electrolytes. It has been observed that the initial total current falls rapidly with time due to the depletion of the ionic species in the electrolyte and becomes constant in the fully depleted situation. Residual current is due to the electron migration across the electrolyte and interfaces. The transference numbers are calculated from the polarization current vs. time plot using the equations:

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

Where I_i is the initial current and I_f is the final residual current.

The ionic transference number (t_{ion}) for all compositions of the PVA: $C_6H_{10}O_4$ electrolyte systems has been found to be in the range 0.93 - 0.95 (Table 1). The charge transport in these polymer electrolyte systems is predominantly ionic accompanied by mass transport and electronic contribution to the total current is negligible (Nithya *et al.* 2007).

4. Conclusion

The proton conducting solid polymer electrolytes composed of Poly vinyl Alcohol (PVA) with different molar concentration of adipic acid ($C_6H_{10}O_4$) have been developed by using solution casting technique.

- XRD analysis confirms the amorphous nature of polymer electrolytes.
- DSC reveals that the addition of adipic acid to pure PVA electrolyte enhances the thermal stability of PVA.
- The highest ionic conductivity has been found to be 7.50 X 10^{-5} Scm^{-1} at 303 K for 75 PVA: 25 $C_6H_{10}O_4$ polymer electrolyte.
- Temperature dependent conductivity of polymer electrolytes shows Arrhenius behavior.
- The best ion conducting sample (75 PVA: 25 $C_6H_{10}O_4$) has the lowest activation energy (0.2744eV) among the prepared samples.
- The transference number of the highest conductivity sample is 0.95 suggesting that the prepared polymer electrolyte is a good proton ion conductor.

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