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Electrical and Optical characterization of pure and doped Poly Vinyl Alcohol polymer electrolytes

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Abstract: Novel proton conducting solid polymer electrolyte membranes based on Poly vinyl alcohol (PVA) with Succinic Acid as dopant are prepared by solution cast technique with varying doping concentrations up to 40 wt.%. The electrical conductivity and optical absorption of pure PVA and doped PVA electrolytes are investigated. DC conductivity behavior is studied in the range 303K to 373K. It is found that PVA: Succinic acid (70:30) electrolytes exhibited the maximum conductivity. The electrical conductivity initially increased with increasing dopant concentration and then showed a decrease beyond 30 wt.% concentration. The increase in conductivity is attributed to formation of charge transfer complexes while the decrease for concentrations above 30 wt.% is due to segregation. Optical absorption studies are made in the wave length range 200-600nm and the values of optical band gap (direct and indirect) are estimated. The results obtained are presented and discussed.

Keywords: Electrolyte membranes, electrical conductivity, optical absorption, Succinic Acid, doped PVA electrolytes, optical band gap.

1. INTRODUCTION

Now-a-days the polymer materials are of large interest because of their low cost, easy process-ability, low weight, high quality surfaces and easy fabrication etc. In recent years, studies on the electrical and optical properties of polymers have attracted much attention due to their applications in optical devices [1, 2]. The optical properties of polymers can be suitably modified by addition of dopant or other polymer with the host [3].

The potential application of ionically conducting polymers as solid electrolytes in a variety of electrochemical devices arises from their advantages such as high energy density, electrochemical stability and easy handling [4]. Within the realm of solid polymer electrolytes, proton conducting polymer electrolytes have received much attention because of their unique application as solid electrolyte in various electrochemical devices such as fuel cells, sensors, electro-chromic displays and windows etc. [5].

The recent challenge is to develop a low cost proton conducting polymer electrolyte with high ionic conductivity, good dimensional and mechanical stabilities. Many researchers have studied the behaviour of proton conducting polymer electrolytes based on the host polymers such as poly (vinyl alcohol) (PVA), poly

(ethylene oxide) (PEO), poly (ethylene imide) (PEI), poly (acrylic acid) (PAA), poly (N-vinyl pyrrolidone) (PVP) [6-13] doped with inorganic acids or ammonium salts. However, proton-conducting polymer complexes with inorganic acids suffer from chemical degradation and mechanical integrity making them unsuitable for practical applications [14]. Therefore, in this paper a novel effort is made to use one of the organic acids like Succinic acid as a dopant to prepare a proton conducting polymer and its electrical and optical characterization is carried out.

2. EXPERIMENTAL
2.1 Preparation of polymer electrolyte films

Pure PVA (Mw 1, 40,000 from AR chemicals) complexed with Succinic acid in various compositions (90:10), (80:20), (70:30) & (60:40) by wt% ratio, are prepared using the solution caste technique. PVA & Succinic acid are dissolved in double distilled water; the solutions obtained are thoroughly stirred for 10-12 hrs to get homogenous mixture. The stirred solution is caste onto polypropylene dishes and allowed to evaporate slowly at 50°C. After one or two days solid polymer layers are formed as thin membrane with nearly 100 microns thickness at the bottom of dishes. These membranes are dried in vacuum (10^{-3} torr) to eliminate the residual traces of water then carefully separated from the dishes and stored in evacuated desiccators.

2.2 Electrical and optical measurements

D.C. conductivity is measured using indigenously built instrument in the temperature range 300-373K with Keithley programmable electrometer (model

No.196). Thickness of the films is measured by Mitutoyo thickness gauge (no.7301, range 0.01mm to 10mm). Optical absorption spectra are recorded at room temperature in the wave length 200-600 nm using optical spectrometer.

3. RESULTS AND DISCUSSION
3.1 Electrical properties

The electrical properties of the polymer electrolyte can be enhanced by modifications to the polymer host or changing the dopant salt/acid or its proportion. In addition to this, they can further be enhanced by supplying thermal energy.

3.1.1 Composition dependence of conductivity.

The influence of the nature and the concentration of the incorporate dopant on the electrolyte is complex. Essentially, polymer electrolyte is formed when the acid/salt consisting of a polarizing cation joins a large anion of delocalized charge to minimize the lattice energy. The dopant affects the conductivity through crystalline complex formation, intra-molecular cross-linking of the polymer chains and the degree of salt dissociation (the number of charge carriers it can provide). When more salt is dissolved in to the polymer matrix, the conductivity increases as a result of addition of charge carriers. As the salt concentration in a solution is increased, the inter-ionic distance decreases and ion-ion interactions become progressively more significant which contribute for enhancement in conductivity.

It is known that in semi-crystalline polymers, the dopant forms Charge Transfer Complex (CTC) and is expected to reduce the barrier between the trapping sites. This reduction in the barrier provides a conduction path through the amorphous regions of the polymer matrix.

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The decrease in the activation energy and increase in the mobility of carriers results in an enhancement of its conductivity [15, 16].

However, as dopant concentration increased above a certain limit, the conductivity reaches a maximum and then falls. It has been deduced that at high dopant concentrations, formation of immobile aggregated regions will contribute to the fall in conductivity (Gray, 1991).

The variation of dc conductivity (σ) as a function of dopant (acid) content by wt% in Poly Vinyl Alcohol (PVA) and Succinic acid at various temperatures is as shown in Fig.1. The increase in the ionic conductivity with the increase in the composition of the dopant is primarily attributed to increased proton carrier concentration. The movement of protons through the polymer matrix is assisted further by the large amplitude of the polymer segmental motion. The segmental mobility of polymer chains is much higher in amorphous regions than in crystalline.
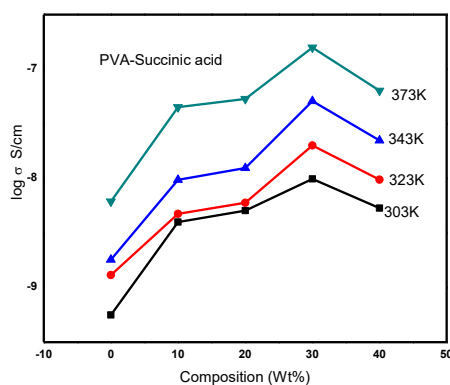
amorphous regions and at the same time reduces the crystallinity. The continuous increase in the conductivity of polymer electrolytes with increasing salt/acid concentration is thus attributed to decrease in the degree of crystallinity. Therefore, conductivity increases as the degree of crystallinity decreases or in other words, as the flexibility of the polymeric backbone increases.

Jeon et al (17) reported that, the conductivity of the polymer electrolytes increased with increasing salt concentration, but further addition of the salt caused the conductivity to decrease. At higher concentrations, the conductivity decreases because of the increasing influence of ion pairs, ion triplets and higher ion aggregations which reduce overall mobility and number of effective charge carriers. This effect is observed for the cases of dopant acid concentration in the region above 30 wt% of salt (acid) in the PVA polymer.

3.1.2 Temperature dependence of conductivity

In general, the temperature dependent conductivity (σ) of polymers may be expressed as in Eqn.1

$$\sigma = (\sigma_o/T) \exp(E_a/kT) \quad - - - - (1)$$

where σ_0 is the pre-exponential factor, E_a the activation energy, k the Boltzmann constant and T is the absolute temperature.

The increase in the conductivity with temperature is also partially due to the transition from crystalline/ semi-crystalline phase to amorphous phase.

FIGURE 1.Composition vs conductivity of PVA: Succinic acid polymer electrolytes with temperature as parameter.

Addition of more acid in to the polymer not only contributes more protons for conduction but also increases the

According to the Vacancy diffusion theory, for the protons to jump from one lattice site to other lattice site, need energy to break bonds with neighbors and to cause the necessary lattice distortions during jump. This energy comes from the thermal energy of atomic vibrations ($E_{av} \sim k_B T$). Due to the thermal energy supplied, a small free volume is created around segments. At low temperatures Arrhenius model was assumed where the cation transport and its contribution to conductivity is a result of cation jump into neighbouring vacant sites and hence, increases the proton conductivity to a higher value [18, 19]. This hopping mechanism between coordinating sites is essentially in the region below T_g.

However, above T_g, no dependency on temperature comparable to Arrhenius behaviour could be obtained. Poly Vinyl Alcohol is a linear polymer with carbon chain as the back bone, the polymer chains which are less entangled are capable of causing electrical conductivity. At temperatures beyond the glass transition temperature T_g, the increase in the conductivity with temperature is mainly due to hopping mechanism between coordination sites, local structural relaxation and segmental motion of polymer [20,21]. As the amorphous region increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favours the hopping inter-chain and intra chain proton movements and the conductivity of the polymer thus becomes appreciably high [22]. Thus it suggests that, the result may be effectively represented by the non- linear dependence and follows the Williams–Landel–Ferry (WLF) mechanism [23]. This mechanism can be better described by Vogel–Tammann–Fulcher (VTF) models and VTF equation.

At the significantly high temperatures (beyond T_g), the polymer can expand easily and produce more free volume which is sufficient to move into the free volume not only for protons but also for solvated molecules or even polymer segments [24]. Therefore, the DC conductivity (log (σ)) versus reciprocal of temperature can be interpreted in terms of the empirical VTF equation. Thus, the result may be effectively represented by Vogel–Tammann–Fulcher (VTF) models and more appropriate to this situation that the behaviour is explained using the Vogel–Tamman–Fulcher (VTF) expression of Eqn.2 corresponding to this region, based on the free volume concept (Kim *et al* 1996).

$$\sigma = AT^{-1/2} \exp(-B/T - T_0)$$
$$- - - - (2)$$

where A and B are constants and T_0 is the reference temperature. Constant A is related to the number of charge carriers in the electrolyte and B is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains.

The variation of dc conductivity as a function of inverse temperature for pure PVA and composite polymer electrolytes with different compositions, of PVA: Succinic acid is shown in Fig.2 in the

temperature range of 298-373K. From the plots the proton conductivity is found to increase with the increase of temperature in pure PVA as well as in all the composite (complexed) polymer electrolytes.
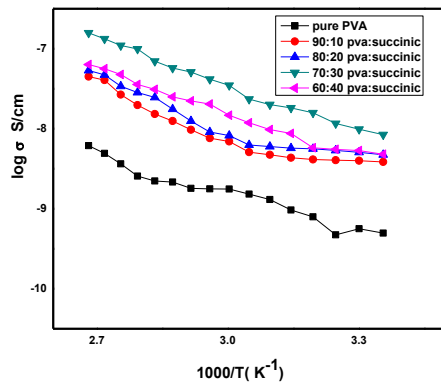

FIGURE.2 Conductivity $\log(\sigma)$ vs 1/T plots for PVA-Succinic acid composite polymers

This is in accordance with the expected behaviour from all materials except metals. From the plots it is observed that at low temperatures, Arrhenius behaviour is exhibited and at high temperatures, VTF (Vogel-Tamman-Fulcher) behaviour is exhibited.

Both the regions correspondingly have two distinct activation energies. A number of other polymer electrolyte systems including those based on PVA [25,26,27,28,29] have also exhibited similar behaviour.

In order to further analyze the conduction mechanism, the activation energies are evaluated for the regions below and above the glass transition temperature T_g using the conductivity plots shown in fig.2. These values are tabulated in the table.1.

TABLE 1. Activation energy values of PVA based polymer electrolytes obtained from DC conductivity.

Polymer electrolyte	σ in S/cm at **303K**	σ in S/cm at **373K**	AE in eV At < T_g	AE in eV At > T_g
Pure PVA	5.62×10^{-10}	6.15×10^{-9}	0.1349	0.611
PVA:Succinic acid (90:10)	3.98×10^{-9}	4.49×10^{-9}	0.417	0.642
PVA:Succinic acid (80:20)	5.07×10^{-9}	5.35×10^{-8}	0.357	0.569
PVA:Succinic acid (70:30)	9.87×10^{-9}	1.58×10^{-7}	0.553	0.425
PVA:Succinic acid (60:40)	5.34×10^{-9}	6.36×10^{-8}	0.514	0.375

From the obtained values of activation energies, it is inferred that both the regions do not exhibit the same behaviour of conductivity as the values are distinct for the two regions and the pattern of variation of these values, with varying dopant concentration, is also different for the region below T_g from the one corresponding to the region above T_g.

3.2 Optical properties

The information about band structure can be studied by an optical absorption. In indirect bandgap semiconductors, the transition of electron from conduction band to valence band is always associated with a phonon of the appropriate magnitude. Davis and Shalliday [30] reported that in polymer electrolytes, near fundamental band edge both direct and indirect transitions occur and can be observed by plotting $\alpha^{1/2}$ and α^2 as a function of energy hν. The relationship in

eqn.3 and eqn.4 are based on the analysis of Thutupalli and Tomlin [31]

$$(h\nu\alpha n)^2 = C_1 (h\nu - E_{gd}) \qquad ---- (3)$$

$$(h\nu\alpha n)^{1/2} = C_2(h\nu - E_{gi}) \qquad ---- (4)$$

for direct and indirect band semiconductors respectively, where $h\nu$ is the photon energy, E_{gd} is the direct band gap, E_{gi} is the indirect band gap, n is the refractive index, α is the absorption coefficient and C_1, C_2 are constants.

The absorption coefficient (α) is calculated from the absorbance (A). The variation in absorbance with wavelength of the incident radiation is shown in fig.3. The absorbance peak has shifted in the case of doped PVA suggesting the occurrence of complexation. After the necessary correction for reflection, the absorption coefficient (α) is determined using the relations in eqn.5 and eqn.6.

$$I = I_0 \exp (-\alpha x) \qquad ---- (5)$$

Hence

$$\alpha = \frac{2.303}{x}\log\left(\frac{I}{I_o}\right) = \left(\frac{2.303}{x}\right)A \qquad ---- (6)$$
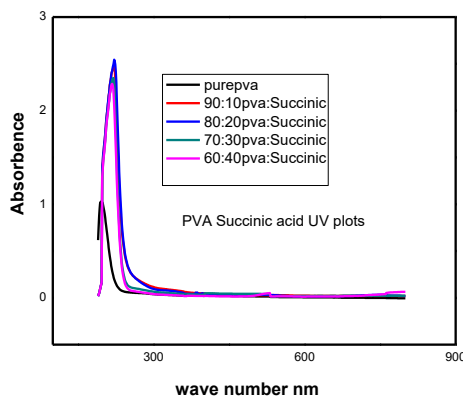
where x is the thickness of the sample.

FIGURE.3 Optical absorption spectra of pure and Succinic acid doped PVA polymer electrolytes

To determine the width of the band gap $(\alpha h\nu)^2$ is plotted as a function of photon energy (hν) and shown in fig.4. The direct band gap value is determined by extrapolating the linear portion of the curve on to the energy axis. The intercept on the x-axis gives the direct band gap energy value.
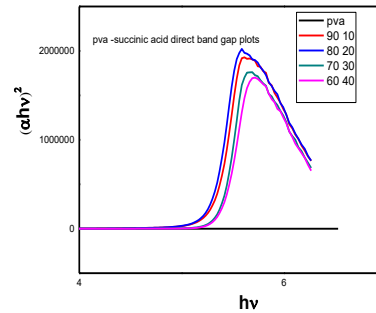

FIGURE.4 $(\alpha h\nu)^2$ vs hν plots of pure and Succinic acid doped PVA polymer electrolytes

When a direct band gap exists, the absorption coefficient has the following dependence, shown in eqn.7, on the energy of incident photon [32, 33]

$$h\nu\alpha = C (h\nu - E_g)^{1/2} \qquad (7)$$

where E_g is the band gap, $C(=4\pi\sigma_0/nc\Delta E)$ is a constant dependent on the specimen structure, α is the absorption coefficient, ν is the frequency of the incident light and h is the Planck's constant. The curves of $(\alpha h\nu)^2$ vs. hν are plotted and the direct band gap values are obtained which are tabulated in the Table2.

For indirect transitions, which require phonon assistance, the absorption coefficient has the following dependency, shown in eqn.8, on photon energy [32, 33].

$$h\nu\alpha = A\,(h\nu - E_g + E_p)^2 + B\,(h\nu - E_g - E_p)^2 \quad ---- (8)$$

where E_p is the energy of the photon associated with the transition and A and B are constants depending on the band structure. Again, the indirect band gap values are obtained from the $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot and is shown in fig.5.
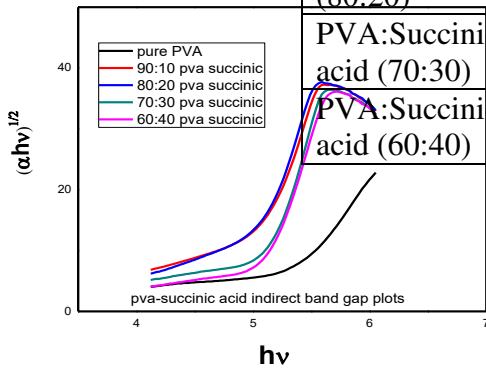

FIGURE.4 $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots of pure and Succinic acid doped PVA polymer electrolytes

Following the same procedure adopted for determining the direct band gap energy, the indirect band gap value is also determined by extrapolating the linear portion of the curve on to the energy axis. The intercept on the x-axis gives the indirect band gap energy value. These values are also tabulated in the table 2.

From the significant values obtained for indirect band gap energies for various polymer electrolyte samples clearly indicate that the samples under consideration exhibit not only direct band gap transitions but also the indirect band gap transitions. It is clear from the table, that the direct band gap and indirect band gap values displayed a decreasing trend on

complexing with dopant acid up to a dopant concentration of 30%wt. This type of behaviour was also observed in many other polymer electrolytes [34-37].

Table 2. Optical band gap values for PVA complexed with Succinic acid polymer electrolytes.

Polymer electrolyte	Direct band gap energy (eV)	Indirect band gap energy (eV)
Pure PVA	5.65	5.20
PVA:Succinic acid (90:10)	5.273	5.156
PVA:Succinic (80:20)	5.185	5.07
PVA:Succinic acid (70:30)	5.150	4.95
PVA:Succinic acid (60:40)	5.161	4.994

The decrease in optical band gap energy on doping, up to a dopant concentration 30 wt.%, may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes (CTCs) in the host lattice [38]. These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice. This

results in a decrease of optical band gap energy.

When the dopant concentration increases further, it leads to segregation of the dopant in the host matrix. These molecular aggregates impede the motion of charge carriers resulting in decreased conductivity and hence increased optical band gap energy.

4. CONCLUSIONS

The conductivity of pure PVA is enhanced by doping with Succinic acid, a member of dicarboxylic acids and one of the organic acids, due to additional protons supplied by the dopant.

It is found that the maximum conductivity and minimum bandgap energy values, for both direct and indirect transitions, are obtained from the complexed PVA with Succinic acid when in 30% wt. proportion.

The DC conductivity of 1.58×10^{-7} S/cm at 373K is an encouraging value which suggests that a complexed solid polymer electrolyte membrane made from PVA with Succinic acid as dopant is a promising candidate for use in an electrochemical cell.

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