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Electrical conductivity, Transport and Discharge characteristics of a sodium acetate trihydrate Complexed with polyvinyl alcohol for Electrochemical cell

SK.Shahenoor Basha[1], G.Sunita Sundari[1], K.Vijay Kumar[1]

Department of Physics, K L University, Guntur-522502 Andhra Pradesh- India.

Abstract: In this present work Poly vinyl alcohol (PVA) based solid polymer electrolyte systems (PVA+ $CH_3COONa3H_2O$) was prepared by solution-cast technique. The crystalline structure and its characteristics were studied by using X-ray diffraction and the complexation between (PVA+ $CH_3COONa3H_2O$) has been observed from FTIR data. The bulk resistance of polymer electrolyte was calculated by using impedance analysis the ionic conductivity of the polymer electrolyte can be calculated by using AC conductivity at 303K room temperature the composition dependence of A.C Conductivity in the temperature range 303K was carried out. And it reveals the conduction mechanism to be the Arrhenius-type thermally activated process. The ionic conductivity of PVA Polymer electrolyte is about $9.73x10^{-9}$S/cm at Room temperature. The highest conductivity is found to be $1.07x10^{-6}$S/cm at 303K, for sample 70:30 of sodium acetate in PVA.The charge transport in the polymer electrolytes was calculated by Wagner's polarization technique. The total ionic transference number was found to be 0.98 in this polymer electrolyte system, which suggest that the charge carriers in these polymer electrolytes are mainly due to ions, By using the solid polymer electrolyte films an electrochemical cell has been fabricated with the parameters of Na/(PVA+$CH_3COONa3H_2O$) /(I+C+electrolyte). And its discharge characteristics were studied, such as open circuit voltage (OCV), short circuit current (SCC) has been calculated.

Keywords: Solid Polymer electrolyte, Solution Casting technique, XRD, FTIR, AC conductivity, transport properties, discharge characteristics, cell parameters.

Introduction:

Solid polymer electrolyte materials have become a great importance which are using in many applications because of their potential applications, such as cell, electro chemical sensors, electro chromic devices, cellular phones, etc[1-2]. Due to their excellent characteristics such as good thermal and mechanical strength, ionic conductivity at ambient temperatures, electro chemical stability and good compatibility with electrodes. The ionic conductivity in solid polymer electrolytes is mainly due to flow of cations and anions in polymer matrix. Now a day’s an effort have done to improve the mechanical strength and ionic conductivity in polymer electrolytes.

In the last few decades an effort has done for the development of gel polymer electrolytes such as polyvinyl alcohol (PVA), poly vinyl pyrrolidine (PVP), polyethylene glycol (PEG), poly acrylonitrile (PAN), poly vinylideneflouride (PVdF). Among the above listed polymers, polyvinyl alcohol (PVA) have been intensively investigated because of its excellent characteristics and its applications.PVA is the good potential materials which are having high storage capacity, high dielectric strength, and electrical properties it has a carbon chain backbone with hydroxyl group attached to methane carbons. These O-H groups can be source of hydrogen bonding and therefore, assists the formation of polymer complex[3] .It has good mechanical properties and shows electronic as well as ionic conduction[4] .Thus in this present paper an attempemt has been made to synthesize and characterization of PVA based sodium acetate salt for battery application.

Experimental Section:

In the present investigation Polyvinyl alcohol (PVA), Sodium acetate trihydrate ($CH_3COONa3H_2O$) and double distilled water were used to synthesis of solid polymer electrolytes.

Synthesis:

For the formation of PVA polymer electrolyte films, Pure PVA (Aldrich ≈ $9x10^{-9}$) is added to the sodium acetate trihydrate ($CH_3COONa3H_2O$) in the different weight ratios (80:20), (70:30), (60:40) and dissolved in distilled water at room temperature for 24 Hrs to get a homogeneous mixture, then the solution is poured on polypropylene dishes and evaporated slowly under vacuum for removal of solvent traces. After drying the films are peeled off and separated from the Petri films. And the films are kept in desiccators until further characterization process.

Measurement Technique:

The solid polymer electrolyte was subjected to X-ray diffraction to study the crystal structure by using PANALYTICALX Petro Powder X-ray diffractometer 30 mA at room temperature in the Bragg angle range 10-70°. Structural morphology of (PVA+$CH_3COONa3H_2O$) has been studied by X-Ray diffractometer. The complex formation between PVAand$CH_3COONa3H_2O$ has been studied from the FTIR data. The A.C conductivity has been measured using the conductivity set up at the room temperature range 303K by using HIOKI 3532-50 LCR Hitester over a frequency range 42Hz -5MHz. The ionic and electronic transport numbers (t_{ion} and t_{ele}) were evaluated by means of Wagner's polarization technique[5],under a DC bias at 1.5V.Electrochemical cell has been fabricated with the configuration of Na/(PVA+ CH_3COONa $3H_2O$)/(I+C+electrolyte). And its discharge characteristics were observed at constant load of 100 KΩ.

Results and Discussion:

XRD Analysis:

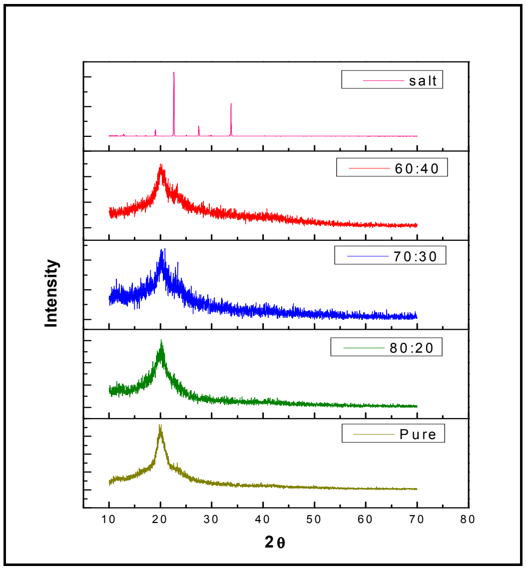

Fig 1XRD of Pure PVA and CH3COONa3H2O doped PVA polymer electrolyte films

The XRD profiles of pure PVA and $CH_3COONa3H_2O$ with different ratios are shown in fig.1. From the figure depicts the XRD pattern of pure PVA shows, and well defined peaks are observed $CH_3COONa3H_2O$ which indicates the crystalline nature of the salt and also a broad peak is observed for Pure PVA corresponds to crystalline orthorhombic lattice which is centered at around 20° [6], and broad peak corresponds to amorphous content lies in between 10° - 30° which corresponds to amorphous content indicating its semi crystalline nature[7]. A slight shift of the peak is also observed at 22°, as the concentration of the salt increasing the XRD peaks increase which indicates the amorphous nature of the polymer. Hodge et.al[8] this amorphous nature indicates that there is a high ionic conductivity, which can be expected in amorphous polymers having flexible back bone[9]. As the intensity of the peak decreases such that there is a percentage of salt is completely mixed with the polymer suggesting a decrease in the degree of crystallinity of the complex[10]. This could be due to the disruption of the PVA polycrystalline structure by $CH_3COONa3H_2O$ salt.

FTIR Analysis:

FTIR spectroscopy is a versatile tool to investigate the polymer structure and gives the information about the structural components, and used to analyze the interactions among various constituents of the polymeric films[11].

These interactions of atoms or ions are having different types of bonds with different natural frequencies. The FTIR spectra of pure PVA and CH3COONa3H2O are shown in fig 2.

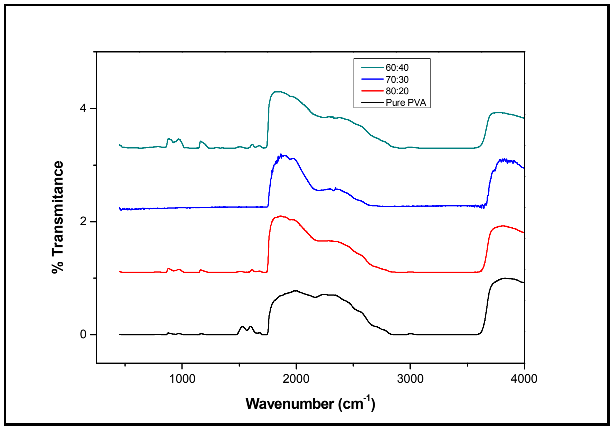

Fig 2 FTIR of pure PVA and CH3COONa3H2O doped PVA polymer electrolyte films

The absorption band is decreasing from 4000-3600 cm^{-1} due to O-H stretching of PVA which is shifted to 2949-1750 cm^{-1} , 1653-1500 cm^{-1},and 1250-700cm-1in 20 wt%, and 30 wt% 40 wt% $CH_3COONa3H_2O$ complexed PVA films respectively. It indicates that there is an interaction between polymer and dopant salt. In pure PVA C-C stretching, C-H stretching of CH_2, C=O are present, which exhibits the absorption peak at 853 cm^{-1} has been assigned to C-H rocking, Due to the increase the salt concentration in the polymer matrix, these bands frequency is decreased and some of the intensity is shifted the CH_2 stretching vibration from 3600-3010where as the band at 3000cm^{-1} indicates that there is an chemical interaction of sodium acetate ions in the PVA matrix. The shift in acetate C–O stretching of PVA from 917 cm^{-1} to 935 cm^{-1},1236 cm^{-1} and 1250 cm^{-1} also supports the interaction of salt with the host matrix. C-C stretching occurring at 1350 cm^{-1} in pure PVA is shifted to 1770 cm^{-1}, 1248 cm^{-1} and 1046 cm^{-1} in 20 wt%, and 30 wt% 40wt% salt complexed polymer electrolyte films respectively[12]. All these changes in the FTIR spectra are clear indications of the complexation of PVA with $CH_3COONa3H_2O$ salt

Ac Conductivity of PVA+ Sodium Acetate:

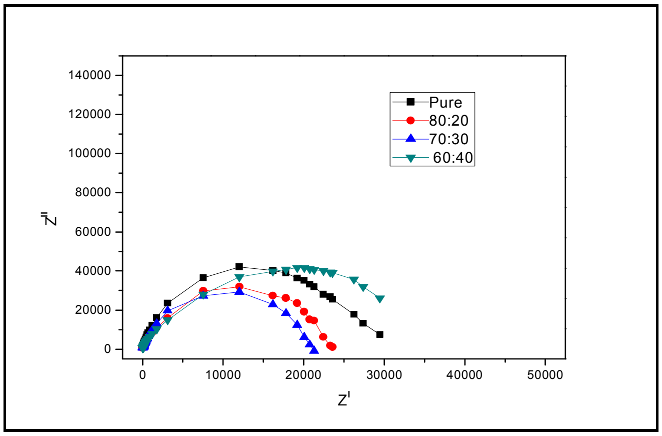

Fig3. Impedance plot for the conductivity of polymer electrolyte PVA:$CH_3COONa3H_2O$ at Room temperature

The conduction mechanism can be calculated by Impedance spectroscopy. Sunandana etal[13] reported that the conductivity mechanism depends on the mobile ion concentration, and it can be investigated from transport properties. The Cole-Cole plots are shown in fig3.Complex impedance plots consists of high frequency semicircle which is related to the conduction process in the bulk of the complex i.e. parallel combination of bulk resistance (due to the drifting of ions), bulk capacitance (due to polymer chain) and a low frequency range, indicates the bulk effect of blocking electrodes i.e. the interface between the electrode and electrolyte is due to the migrations of ions[14].The bulk resistance (R_b)of polymer electrolyte for all samples was calculated from the interception of the semicircular arc on the real impedance (z^1) axis. With the increase of salt concentration the bulk resistance decreases. This may be due to the increase in the mobile charge carriers by the addition of salt. The ionic conductivity increases with increasing CH3COONa3H_2 O content from 20 wt% to 40 wt% Conductivities of the film at Room temperatures were calculated using the formula $\sigma=L/R_b A$, where L is the thickness of the sample and A is the electrode area

Table1. Conductivity, Activation Energies and Transference numbers of (PVA+$CH_3COONa3H_2O$) Electrolyte System.

Films	conductivity at RT (s/cm)	Transference numbers	
		t_{ion}	t_{ele}
Pure PVA	$9.73\text{x}10^{-9}$	--------	-------
PVA+CH_3COONa(80:20)	$1.27\text{x}10^{-7}$	0.96	0.04
PVA+CH_3COONa(70:30)	$1.41\text{x}10^{-6}$	0.97	0.03
PVA+CH_3COONa(60:40)	$1.07\text{x}10^{-6}$	0.98	0.01

Table 2. The values of mobility and transference number for pure PVA and PVA+$CH_3COONa3H_2O$ Electrolyte Systems

Electrolytes	Transference number (t_{ion})	Mobility (μ) (in (m^2/Vs)
Pure PVA	---------	$0.94\text{x}10^{-8}m^2/Vs$
PVA+CH_3COONa(80:20)	0.96	$1.12\text{x}10^{-8}m^2/Vs$
PVA+CH_3COONa(70:30)	0.97	$2.07\text{x}10^{-8}m^2/Vs$
PVA+CH_3COONa(60:40)	0.98	$2.37\text{x}10^{-8}m^2/Vs$

The ionic conductivity of polymer electrolyte of sodium acetate at room temperature 303K is as shown in fig 3. Pure PVA shows ionic conductivity at ($\sigma=5.92\text{x}10^{-9}$ S/cm),at room temperature by adding the salt 30% the ionic conductivity increases to $1.410\text{x}10^{-6}$s/cm, it is due to Hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer chains are the essential to assure high conductivity of the electrolyte[15-16] . The conductivity values of the polymer electrolytes at room temperature are given in Table 2, at RT.

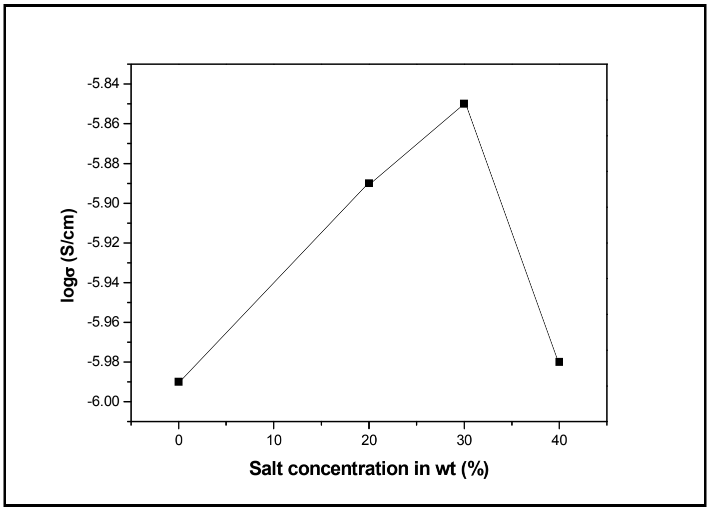

Fig 4.Effect of salt concentration on the conductivity of PVA

Electrical conductivity of pure and $CH_3COONa3H_2O$ doped polymer electrolytes was measured at room temperatures for doped samples. The variation of electrical conductivity as a function of inverse temperature for pure (PVA+ $CH_3COONa3H_2O$) (70:30) was shown in Fig4. The linear variation in vs plot suggests an Arrhenius type thermally activated process represented by the relation

Initially by adding the salt concentration the conductivity also increasing, because of the charge carriers increasing but at high concentration the conductivity of the compositions decreases due to an effect of ion saggregations and higher ion pairs which decreases the mobility and charge carriers. The data reveals that the conductivity of pure PVA is $10^{-9}Scm^{-1}$at RT and its value increases sharply to $10^{-6}Scm^{-1}$.

In general as the conductivity for 70:30 increases the sharp peaks of the salt crystallinity decreases. The crystallinity in the salt the moment of ions obstructs by blocking its path, but there is an increasing of amorphous region due to its free volume this is due to the motion of an ionic charge, migration of ions through the amorphous region.

Transference Numbers:

The electronic and ionic transference number measurement of the mobile species has been evaluated in the polymer electrolyte by using Wagner's Dc polarizing technique. This method was used to analyze the transfer of ions and electrons in a solid polymer electrolyte. By fixing the DC voltage across the sodium (anode)/polymer electrolyte/Carbon powder, electrolyte film (cathode), the polarization current was calibrated as a function of time on the application of the cell with 2.5 volts across the cell. The current vs time plots were obtained and shown in fig 5. Hence the transference number of electronic and ionic measurement plays a major role in explaining the conductivity values in solid polymer electrolytes[17].The transference number (t_{ion} and t_{ele}) were calculated by using the equations and the resulting data values is given in the tables

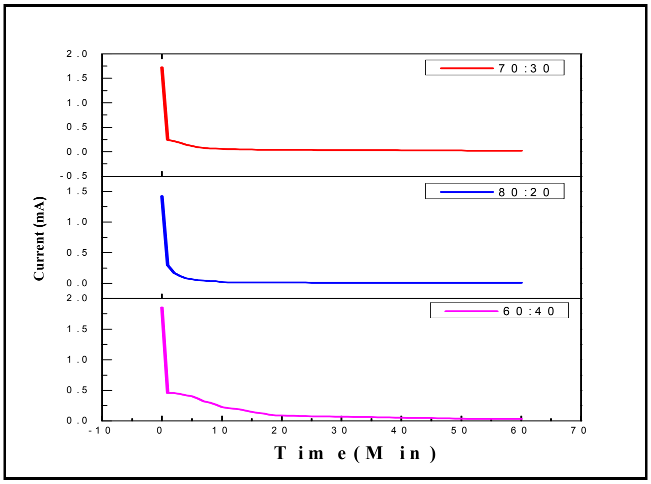

Fig5. Transference plots of PVA: $CH_3COONa3H_2O$ polymer electrolyte for different composition ratios

$t_{ion} = i_t - i_{ele}/i_t$ **and** $t_{ele} = i_{ele}/i_t$

Where i_t is the initial current and i_{ele} is the final residual current Since the ionic transference number (t_{ion}) values are lies in between the range 0.96-0.98. the ionic transfer number (t_{ion}) for PVA+$CH_3COONa3H_2O$ solid polymer electrolyte was found to be ~0.98 .This suggests that the charge transport in these polymer electrolyte films are mostly due to ions only a negligible contribution comes from electrons. Mobility of the ionic species of solid polymer electrolytes were calculated by using transient ionic current method .The mobility of ions in SPE is determined using the equation

$\mu = d^2/TV$

Where d is the thickness of the sample, T is the time of flight and V is the applied voltage (2.5V). The calculated mobility is found to be $2.37 \times 10^{-8} m^2/Vs$ at (70:30) for PVA+$CH_3COONa3H_2O$.

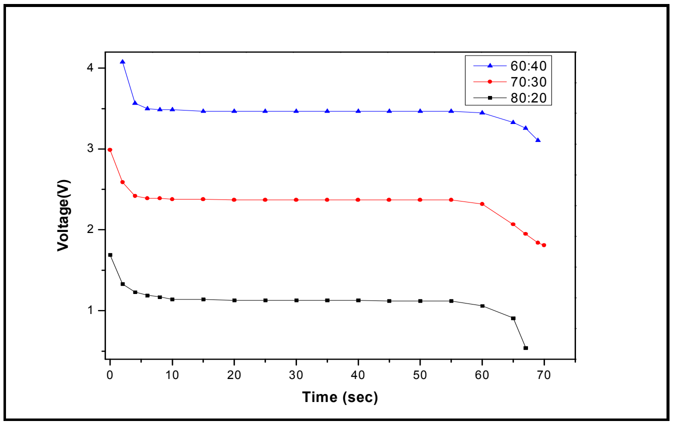

Fig6. Discharge characteristics of PVA: $CH_3C00Na3H_2O$ electro chemical cell at a constant load of 100KΩ

Discharge characteristics

Discharge cell Solid polymer electrolyte were fabricated by Na/[PVA+$CH_3C00Na3H_2O$](70:30)/(I_2+C+electrolyte) at room temperature at a constant load of 100KΩ.are shown in fig. it is observed that there is an initial sharp decrease of voltage. It may due to the polarization and/or the formation of thin layer of sodium salt at the electrode /electrolyte interface. The discharge parameters of the cell were evaluated. Hence this cell parameter of the polymer electrolyte was calculated with the other cell parameters and is listed below table3.

Table3. Cell parameters of Na/[PVA+$CH_3C00Na3H_2O$]/ (I_2+C+electrolyte)

Cell parameters	PVA+$CH_3COONa3H_2O$ (80:20)	PVA+$CH_3COONa3H_2O$ (70:30)	PVA+$CH_3COONa3H_2O$ (60:40)
Cell weight (g)	1.75	1.8	1.83
Area of the cell (cm^2)	1.31	1.31	1.3
Open circuit voltage (OCV)	1.8	1.9	2.1
Discharge time (Hrs)	72	75	70
Current density ($\mu A/cm^2$)	94.2	102.84	212.95
Discharge cell (µA/h)	1.35	1.42	1.57
Power density (W/Kg)	0.28	0.35	0.42
Energy density (W h/Kg)	16.98	39.54	68.75

Table 4: cell parameters of polymer electrolyte batteries

Solid state electro chemical cell	Opencircuit voltage (OCV)	(V)Discharge time for plateau region (h)	References
Na/(PVA + NaF)/(I2 + C + electrolyte)	2.53	112	28
Mg/(PVA+Mg(CH3COO)2)/(I2 + C+electrolyte)	1.84	87	16
Mg/(PEO +Mg(NO3)2)/(I2 + C + electrolyte)	1.85	142	3
K/(PVP+PVA+KClO3)/(I2 + C + electrolyte)	2.00	52	29
K/(PVP + PVA + KBrO3)/(I2 + C + electrolyte)	2.30	72	30
Mg/(PEG + Mg(CH3COO)2)/(I2+ C +electrolyte)	1.84	32	31
Ag/(PEO + AgNO3)/(I2 + C + electrolyte)	0.595	48	32
Na/(PVA + $CH_3COONa3H_2O$)/(I2 + C + electrolyte)	1.9	75	present

Conclusions:

XRD analysis indicates that there is a change from crystalline to amorphousity, with an increasing of $CH_3COONa3H_2O$ salt concentration in the solid polymer electrolytes. FTIR states that the complexation between the salt and polymer. The PVA+$CH_3COONa3H_2O$ (70:30) complexed solid polymer electrolyte, the highest conductivity was found to be $1.41x10^{-6}$S/cm at temperature 303K and the transference of ionic and electronic numbers are found to be in the range 0.96-0.98, this suggests that the charge transport in these polymer electrolyte films are mainly due to ions rather than electrons. By using these polymer electrolyte films an electrochemical cell has been fabricated and their discharge characteristics were studied.

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