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Development of PVP based polymer electrolytes for solid state battery applications

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Abstract

Poly vinyl pyrrolidone (PVP) based polymer electrolyte films complexed with potassium chloride (KCl) salt were prepared using solution casting technique. Structural and complexation of the polymer was confirmed by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) techniques .The temperature dependence of conductivity was performed using AC Impedance Analyzer in the frequency range 0.01- 100 kHz and temperature range 300- 360 K. The transference numbers were determined using Wagner Polarization technique and dominant conducting species were found to be ions rather than electrons. Solid state batteries were fabricated with the configuration K/ (PVP+KCl)/ (I_2+C+electrolyte) and various parameters of the cells including open circuit voltage (OCV), short circuit current (SCC) were evaluated at constant load 100 kΩ.

Keywords: Polymer electrolytes, XRD, FTIR, conductivity, transference numbers, electrochemical cells

Introduction

The study of ionic conductivity in polyether-based hosts complexed with alkali metal salts by Fenton et al. [1] and Wright [2] has generated research activities leading to significant advances in the material characteristics of these polymer-salt complexes and also in their structure. Lithium-ion conducting polymer electrolytes are of great research interest owing to their possible application to lithium-polymer batteries with high-energy density [3]. Among the various types of polymer electrolyte systems used in lithium polymer batteries, solid polymer electrolytes (SPEs) have many advantages such as high ionic conductivity, high-energy density, leak proof, solvent-free condition, wide electrochemical stability windows, easy process ability and light weight. Till now different polymers, such as PAN [4], PMMA [5] and PVdF [6], were studied with these advantages in mind. A few attempts have tried polymer electrolytes based on potassium ion complexed films [7-8]. The main advantage of using potassium metal ion is its availability in abundance at a cheaper cost than lithium. Further, more softness of the material makes it easier to achieve good contact with other components in the battery. In the present investigations, our intension is mainly focused on the preparation and characterization of PVP based polymer electrolytes using potassium chloride as dopant and verifying its potential for the usage of solid state batteries.

Experimental

Films of pure PVP and KCl salt complexed were prepared with weight percent ratios (95:05), (90:10) and (85:15) by solution cast technique using triple distilled water as solvent. The solutions were stirred for 10-12 hours to get a homogenous mixture and then casted on to polypropylene dishes and allowed to evaporate slowly at room temperature. The final product was vacuum dried thoroughly. The XRD patterns of the films were recorded with a Seifert-3003 TT X-ray diffract meter. FTIR spectra of these films were recorded using EO-SXB IR spectrometer with a resolution of 4 cm^{-1}. The measurements were taken over a wave number range of 400-4000 cm^{-1}. AC Impedance measurements were carried out by a computer controlled phase sensitive multimeter (PSM1700) in the frequency range 0.1 kHz -1MHz and temperature range 300- 360 K.

Results and Discussion

XRD analysis

X-ray diffraction pattern is essential to obtain the detailed structure, knowledge on the given material. If the material under investigation is crystalline, well defined peaks are observed, while non-crystalline or amorphous systems show a broad instead of well defined peaks.The X-ray diffraction pattern of pure PVP, potassium chloride salt and PVP complexed with KCl were shown in Fig. 1. In the figure, the pure PVP shows a characteristic peak at14^0 indicating its semi crystalline nature. The intensity of this peak gradually decreases with the increase of potassium chloride salt. This could be due to the disruption of the PVP crystalline structure by KCl. This shows a decrease in the degree of crystallanity of polymer after the addition of salt. No sharp peaks were observed for higher concentrations of KCl salt in the polymer, suggesting the dominant presence of amorphous phase [8].

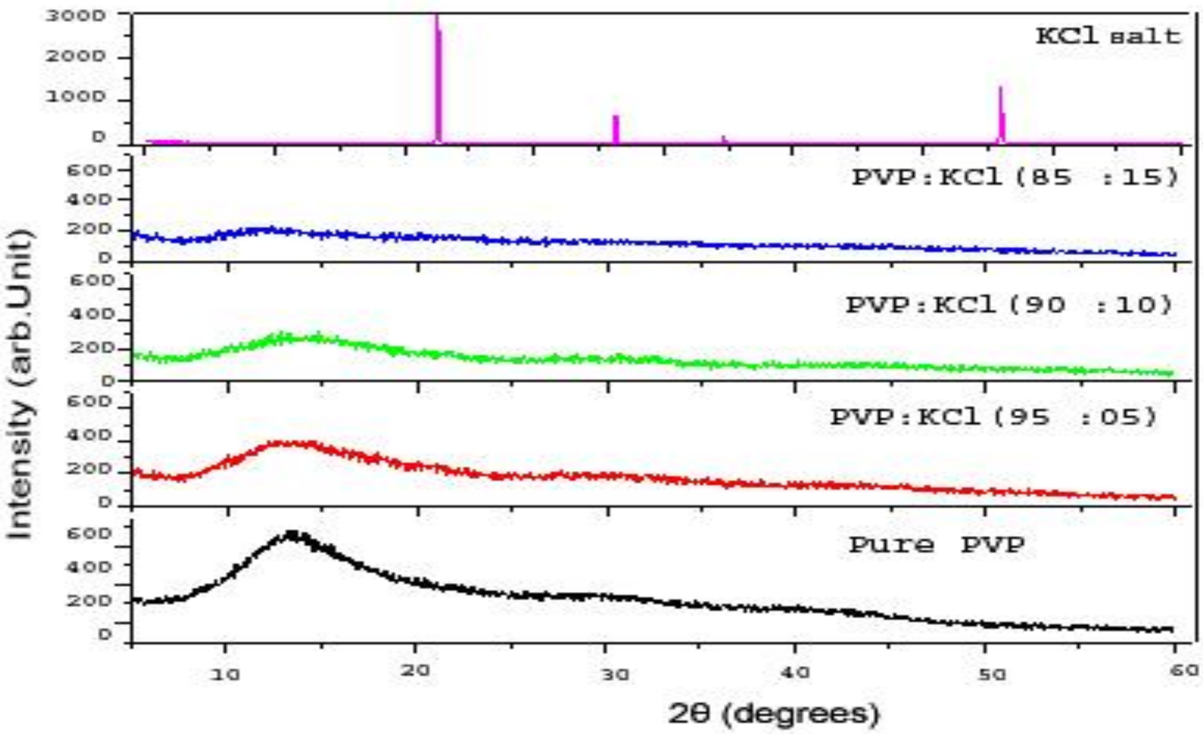

Fig 1: XRD analysis of PVP, KCl and KCl doped PVP polymer electrolyte films

FTIR studies

FTIR spectroscopy is important tool to investigate the information about the complexation and interactions between the various constituents in the polymer electrolyte. Fig.2 shows the FTIR spectra of pure PVP, KCl complexed PVP and KCl salt. The absorption band in the region 2874cm^{-1} is due to the intermolecular hydrogen bonded with carbon C-H stretching frequency of pure PVP which is shifted to 2922 cm^{-1},2939 cm^{-1} and 2952 cm^{-1} in the 05%, 10%, and 15% salt complexed PVP films respectively. In addition to this, the C-N stretching showed an absorption band at 2151 cm^{-1} in pure PVP and is shifted to 2137 cm^{-1}, 2131 cm^{1}and 1878 cm^{-1} for 05%, 10% and 15% salt complexed PVP films respectively. Similarly for C=O stretching for pure PVP is 1750 cm^{-1} and is shifted 1752 cm^{-1} , 1755 cm^{-1} and 1760 cm^{-1} for 05%, 10% and 15% salt complexed PVP films The C-C stretching for pure PVP is 1704 cm^{-1} for Pure PVP and is shifted to 1710 cm^{-1} 1713 cm^{-1} and 1716 cm^{-1} for 05%, 10% and 15% salt complexed PVP films. The C-H bending in pure PVP exhibited absorption at 1465 cm^{-1} is also shifted to1459 cm^{-1}, 1453 cm^{-1}, and 1439 cm^{-1} for 05%, 10% and 15% salt complexed PVP films .Finally the deformation is coupled to C-H wagging and gives rise to a peak at 1382 cm^{-1} in pure PVP which is shifted to 1374 cm^{-1}, 1370 cm^{-1} and 1368 cm^{-1} in the complexed films due to complexation of salt. All these changes in the FTIR spectra are clear indications for the complexation of PVP with KCl salt.

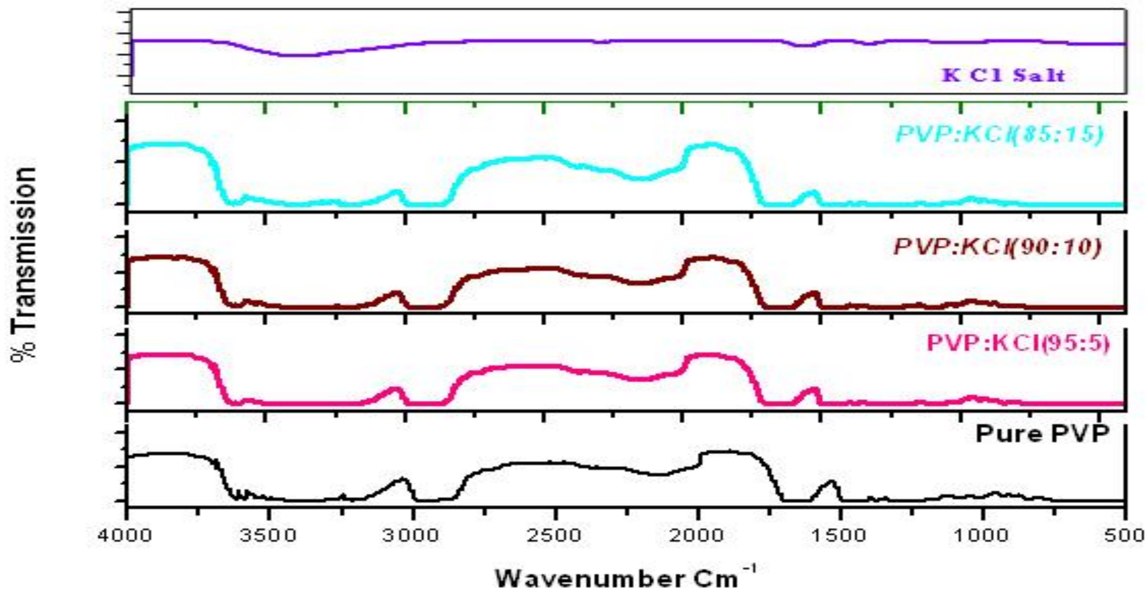

Fig.2 Fourier Infrared Spectra of KCl complexed PVP Polymer electrolyte films.

Impedance analysis

The conductivity of the polymer electrolyte was calculated from the measured resistance, area and thickness of the polymer film, according to the formula:

$$\sigma = l / R_b A$$

where l is the thickness (cm) of the polymer electrolyte, A the area of the blocking electrode (cm^2), and R_b is the bulk resistance of the polymer. Fig .3shows the typical real (Z') and imaginary (Z") parts of the impedance data plotted in complex impedance plane for (PVP+KCl) (90:10) doped polymer electrolyte film at different temperatures. The complex impedance diagram shows two well defined regions, the high frequency region semicircle which is due to the bulk effect of the electrolyte and the linear region in the low frequency range that is attributed to the effect of the blocking electrodes. In an ideal case at low frequency, the complex impedance plots should show the straight line parallel to the imaginary axis, but the double layer at the blocking electrodes causes the curvature [9]. The bulk electrical resistance (R_b) of the material is obtained from the Cole-Cole plots with the intercept of the high frequency side on the X-axis. The bulk resistance decreases with increasing temperature. The decrease in resistance of the polymer electrolyte is due to the enhancement of the ionic mobility and the number of carrier ions with temperature [10]

Fig .4 shows the variation of log (σ) with inverse absolute temperature for various PVP: KCl complexes. From the figure, the conductivity was found to increase with the increase of temperature. This can be explained on the basis of the free volume model [11] and Hopping of charge carriers between the localized states .Since Poly vinyl pyrrolidone is a linear polymer with carbon chain as the back bone, the polymer chains which are less entangled are capable of causing electrical conductivity. Further PVP being a polar polymer, ionizes the KCl salt into anions and cations under the influence of the applied electric field and temperature. These ions hop between the localized states and cause the enhanced conductivity. Further, when temperature increases, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur .Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence the conductivity. Hence, the increment of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobility. The amorphous nature also provides a bigger free volume in the polymer electrolyte system upon increasing temperature. [12].

The activation energies were calculated from log σ vs. 1000/T plots using the following Arrhenius equation.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$

where σ_0 is a constant, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. These values are tabulated in table 1. The low activation energy for potassium ion transport is due to dominant presence of amorphous nature of polymer electrolyte that facilitates the fast K^+ ion motion in polymer network.

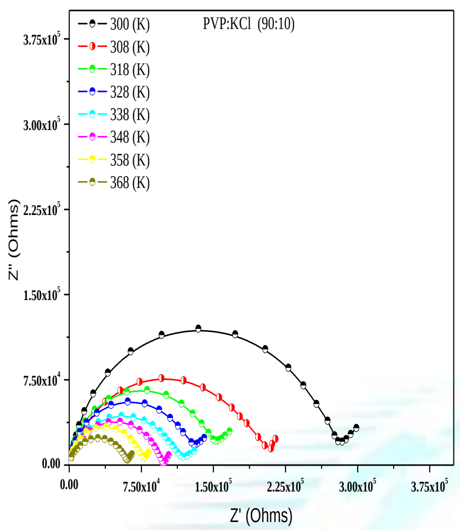

Fig 3: Cole-Cole plot for PVP: KCl (90:10) at different temperatures

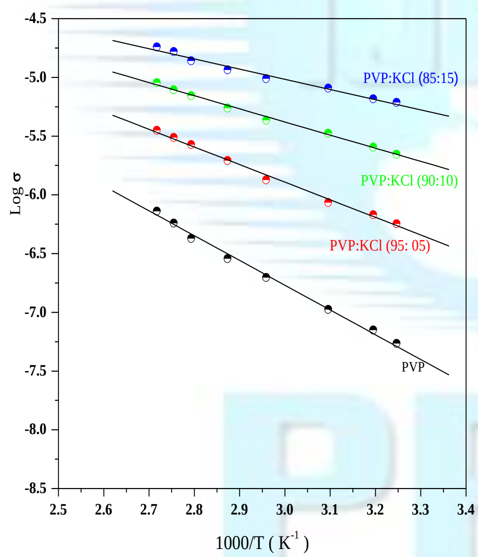

Fig 4: Variation of log σ vs. 1000 / T for pure PVP as well PVP: KCl at different weight percent ratios.

Transference Number Measurements

In order to verify the dominant conducting species in the present electrolyte system, Transference number measurements were carried out using well known Wagner's polarization technique [13]. In this method, the dc current was monitored as a function of time on application of a fixed dc voltage of 1.5 V across the cell K/(PVP + KCl)/C. The current vs. time plot of (PVP + KCl) is shown in Fig. 5. From the figure, the transference numbers (t_{ion} and t_{ele}) have been evaluated using the formula

$$t_{ion} = 1 - I_f/I_i$$

$$t_{ele} = 1 - t_{ion}$$

where I_i and I_f are the initial and final currents, respectively. The resulting data are shown in table 2 for all the compositions of the (PVP: KCl) electrolyte system, the values of the ionic transference number are close to unity. This suggests that the charge transport in these polymer electrolyte films is predominantly to ions rather than electrons.

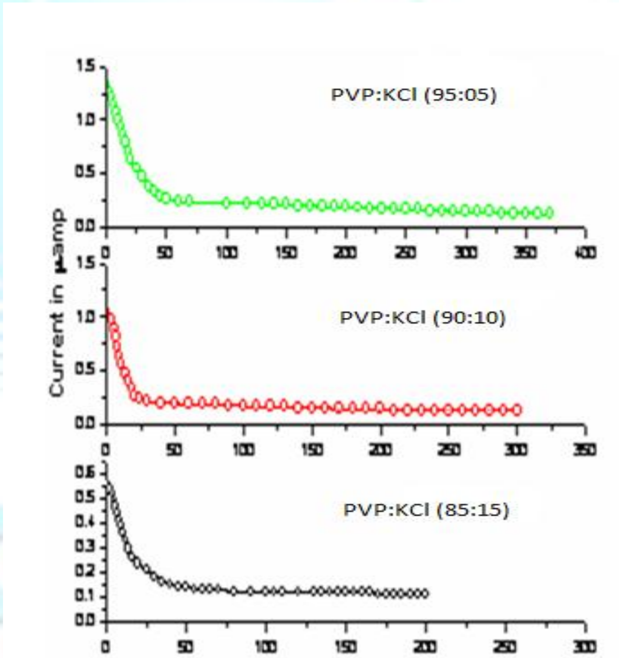

Fig 5: Transference number measurements for PVP: KCl doped polymer electrolyte films

Battery discharge characteristics

The discharge characteristics of the cell K/(PVP + KCl) / (I_2 + C + electrolyte) at an ambient temperature for a constant load 100 kΩ is shown in Fig.6 . The initial sharp decrease in the voltage and current in these cells may be due to polarization and/or to the formation of a thin layer of potassium at the electrode - electrolyte interface. The cell parameters like open circuit voltage (OCV), short circuit current (SCC), current density, power density etc., were evaluated for all the batteries and are given in table 3. From the table it is clear that, cell with the composition (PVA: KCl) (85:15) exhibits better performance and stability than the other compositions. These results are in well comparison with the existing reports and are even better [14-15].

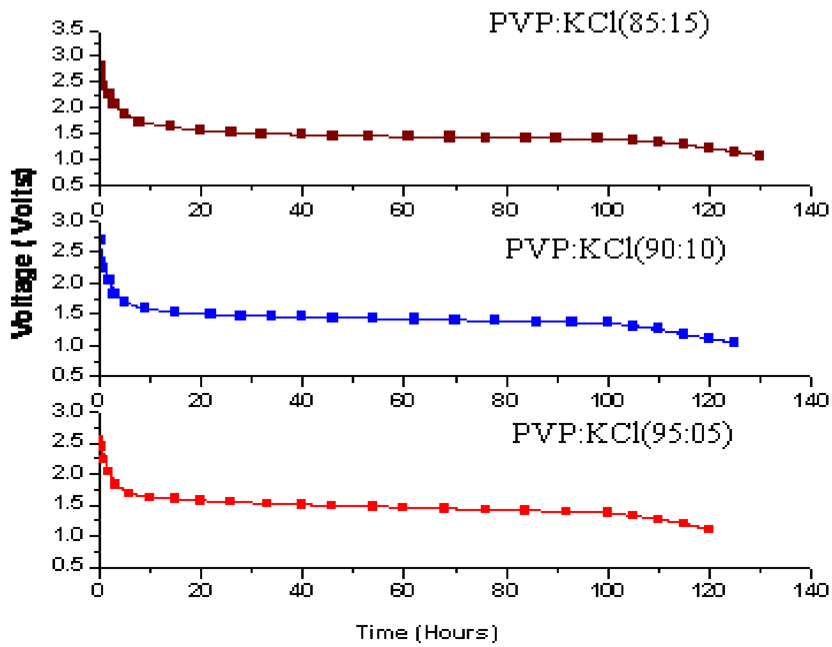

Fig: 6 Discharge characteristics of PVP: KCl doped polymer electrolyte films

4. Conclusions

The XRD pattern reveals the increase in amorphous nature of the film with the addition of salt. The electrical conductivity was found to increase with the increase of temperature. From transference measurements it is clear that, the conduction mechanism in these electrolyte systems is predominantly due to ions rather than electrons. Using (PVP: KCl) polymer electrolyte systems, solid state batteries were fabricated and their discharge characteristics were studied.

Among these cells, the cell made up of (PVP: KCl) (85:15) electrolyte was found to be more stable than the other two cells.

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Table: 1 Activation energies of KCl doped PVP polymer electrolyte films

Polymer electrolyte	Composition	Activation energy (eV)
PVP	----	0.452
PVP+KCl	(95:05)	0.422
PVP+KCl	(90:10)	0.401
PVP+KCl	(85:15)	0.385

Table: 2 Transference numbers of KCl doped PVP polymer electrolyte films

Polymer electrolyte	Composition	Transference numbers	
		t_{ion}	t_{ele}
PVP	--		
PVP+KCl	(95:05)	0.94	0.06
PVP+KCl	(90:10)	0.95	0.05
PVP+KCl	(85:15)	0.96	0.04

Table: 3 Cell parameters of KCl doped PVP polymer electrolyte films

Cell parameters		**(PVP+KCl) (95:05)**	**(PVP+KCl) (90:10)**	**(PVP+KCl) (85:15)**
Open circuit voltage	(V)	2.55	2.78	2.80
Short circuit current	(μA)	785	910	995
Area of the cell	(cm^2)	1.32	1.32	1.32
Weight of the cell	(g)	1.12	1.13	1.15
Discharge time for plateau region	(hours)	103	107	112
Current density	($\mu A cm^{-2}$)	594.69	689.39	753.78
Power density	($W\ kg^{-1}$)	1.787	2.238	2.422
Energy density	($Wh\ kg^{-1}$)	184.06	239.46	271.26
Discharge capacity	($\mu A\ h^{-1}$)	7.621	8.504	8.88