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SPECTROSCOPIC PROPERTIES OF PVP BASED COMPOSITE POLYMER ELECTROLYTE FILMS FOR SOLID STATE BATTERY APPLICATION

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ABSTRACT

Ion conducting polymer electrolyte films were prepared by doping nano-sized TiO_2 particles on PVP (poly vinyl pyrrolidone) complexed with $MgSO_4.7H_2O$ salt by solution casting technique. The structural characteristics for the films were confirmed by X-ray diffraction. The chemical complexation was analyzed by FTIR spectrometer. The ionic conductivity seems to be the Arrhenius-type of thermally activated process. The conductivity of PVP Polymer electrolyte is about 1.02 x 10^{-9} S/cmat room temperature. As increase in the salt $MgSO_4.7H_2O$ percentage with the doping of TiO_2 the conductivity enhanced and it is found to be 1.21 x 10^{-4} S/cm at 373 K for 80:20 composition. The transference number is calculated by using Wagner's polarization technique and it confirms that the doped nano-sized polymer electrolyte film for 80:20 composition charge transport takes place mainly due to ions and negligible charge carriers by the electrons. The total ionic and electronic transference number was found to be 0.98 and 0.02 in these solid polymer electrolyte films. By using these polymer electrolyte films a solid state battery has been fabricated and discharge characteristics were studied under constant load of 100 kΩ. Various cell parameters such as open-circuit voltage (OCV), short circuit current (SCC), energy density and power density has been calculated.

Keywords: XRD, FTIR, dc conductivity, Transport Properties and Discharge Characteristics.

INTRODUCTION

In recent years tremendous effort has been made in the preparation of solid polymer electrolytes. The first theoretical study of solid polymer electrolytes (SPE's) was carried out by Wright and co-workers[1,2] and was devoted to ionic nature of conducting material. The solid polymer electrolyte plays an important role and is used in high energy batteries, fuel cells, sensors, display devices etc. The Recent research trends in the field of rechargeable lithium batteries are directed towards the development of cells with high-energy density (Wh/kg) and high-power density[3]. In this view polymers are being complexed with inorganic salts for increasing the high performance in energy storage devices. These polymer electrolytes show high ionic conductivity for dopant salts. Due to this lack, an effort has done in developing of new polymer electrolytes having high mechanical, thermal, electrochemical stability and high ionic conductivity[4]. The polymer electrolytes show high ionic conductivity by adding dopant salt and the conductivity is related to the glass transition temperature T_g as well as inter-linking of the polymer chain. Pandey et al. has prepared magnesium ion conducting gel polymer electrolytes dispersed with fumed silica for rechargeable magnesium battery application[5]. Chu and Jaipal Reddy studied the PEO-Mg polymer electrolyte system[6]. Metal oxides play a very important role in many areas of chemistry, physics and materials science. The metal elements are able to form a large diversity of oxide compounds. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices and fuel cells, coatings for the passivation of surfaces against corrosion and as catalysts[7-17]. Rao et al.have reported their work on different oxide materials in their earlier studies[18-21].

Poly (vinyl pyrrolidone) (PVP) is a synthetic biodegradable polymer and it deserves a unique attention among the conjugated polymers due to its easy processibility, moderate electrical conductivity and rich in charge transport mechanism. Both these polymers are environmentally friendly and having high polar side groups. PVP is the second polymer, which deserves a special attention among the conjugated polymers because of its good environmental stability and easy processibility. The local modification of the chemical structure induces drastic changes in electronic properties. SPEs based Mg^{2+} ion-conducting salts have attracted considerable attention in the recent years as promising candidates for fabricating all-solid-state electrochemical power sources. The present day scenario in the field of battery technology is that most of the commercially available solid state rechargeable batteries are based on Li/Li^+- ion SPEs.

In the present work, ion conducting polymer electrolytes were prepared polyvinyl pyrolidone complexed with $MgSO_4.7H_2O$ and doping of TiO_2 by solution casting technique. Various experimental techniques have performed to characterize the films such as XRD, FTIR, dc conductivity and transport studies.

EXPERIMENTAL

PVP based solid polymer electrolyte films doped with pure magnesium sulphate hepta hydrate were prepared in the different ratios (95:5), (90:10), (85:15) and (80:20) by using solution casting technique with double distilled water as a solvent. Various concentrations of PVP and $MgSO_4.7H_2O + TiO_2$ are mixed thoroughly. The mixture of these solutions was stirred for 48 hours to obtain a homogeneoussolution. Later the homogeneous solution was pouredin polypropylene dishes and placed to evaporate slowly at room temperature under vacuum drying process to remove the solvent traces. The thin films were peeled off from the dishes and then placed in a desiccator until further test. The thickness of the obtained films was in the range of 90-120 μm.

The obtained dried thin films were characterized by XRD and FTIR. The structural characteristics of the films were determined by XRD using Philips X"pert PRO (Almelo Netherlands) in the range 20°-90°. The FTIR spectra were recorded with the help of Perkin Elmer FTIR spectrometer in the range 4000 to 500 cm^{-1}. The chemical complex formation of the solid polymer electrolyte has been studied with the FTIR data.

RESULTS AND DISCUSSIONS

XRD Studies

XRD Pure PVP shows sharp peaks which determine the semi crystalline nature. While increasing the salt percentage to the polymer the intensity of the peaks is gradually decreased. Hodge et al. who established a correlation between the degree of crystallinity and the intensity of the peak[22]. At 34° a small sharp peak is obtained, it is due to the addition of TiO_2 nano particles to the polymer. As shown in the above Fig.-1, if the intensity of the peak decreasing then it is evident that the salt percentage in the sample is completely mixed with the polymer suggesting a decrease in the degree of crystallinity of the complex.

FTIR Studies

Fourier transform infrared (FTIR) spectroscopy is a promising tool used to analyze the chemical structure and the complexation phenomenon of polymeric materials, nature of functional group and also identifying the formation of new bonds, vibrational modes on the polymeric films. The FTIR spectra of pure PVP, doped with nano particles with $MgSO_4.7H_2O$ with different ratios in the wave number range 400-4000 cm^{-1} are shown in Fig.-2.

The vibrational band is observed at 1500, 3500, 3700, 3800 cm^{-1} are assisted to aliphatic C-H stretching, C-H_2 bending, CH_2 wagging and CN stretching of pure PVP[23]. The bands in the wave number range 1500 -1600 cm^{-1} are obtained due to C-H stretching, C-H_2 bending of PVP respectively. The bands in the wave number range 3500-3800 cm^{-1} corresponding to O-H stretching vibration represents the hydrogen bonding nature for pure PVP. Similar stretching vibrations do not occurs for other polymer complex films. The vibrational bands of pure PVP at 1500, 3500 and 3800 cm^{-1} are shifted to lower frequency and the peak intensity decreases with increase in the salt concentration. The band at 1500 cm^{-1} indicates that there is a possible chemical interaction between the polymer and dopant salt. These shifts in the bands may be attributed to the complex formation between solid polymer electrolytes.

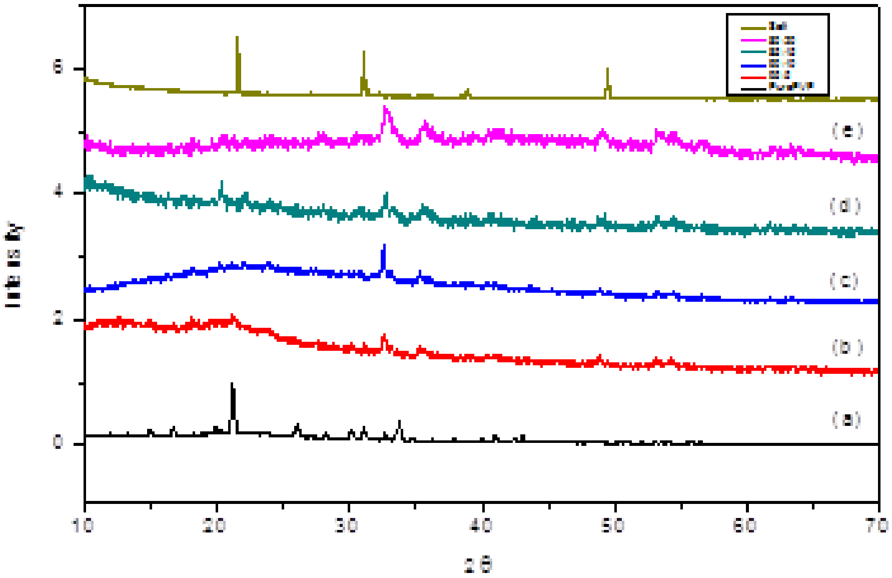

Fig.-1: XRD spectra of (a) Pure PVP (b) PVP+$MgSO_4.7H_2O$+TiO_2 (95:5); (c) PVP+$MgSO_4.7H_2O$+TiO_2 (90:10) (d) PVP+$MgSO_4.7H_2O$+TiO_2 (85:15); (e) PVP+$MgSO_4.7H_2O$+TiO_2 (80:20)

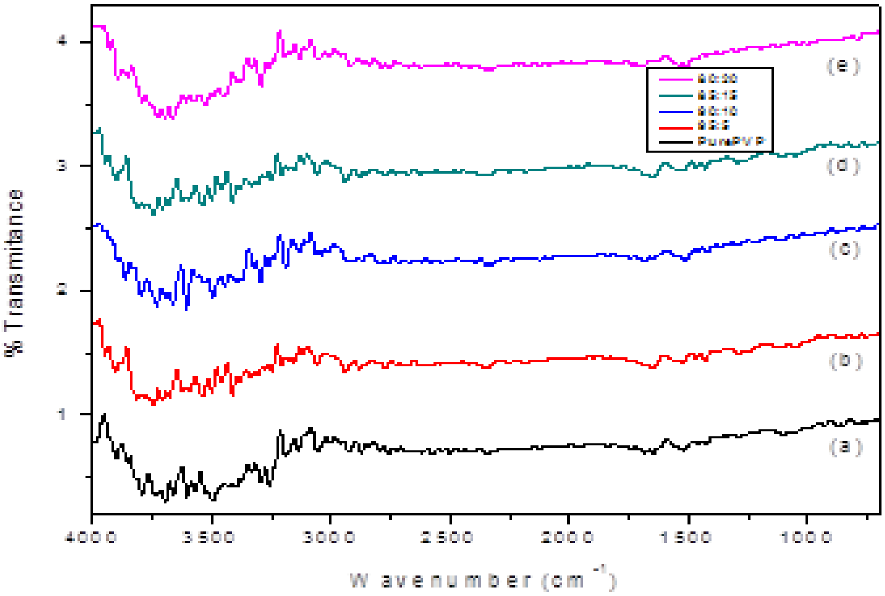

Fig.-2: FTIR Spectra of (a) Pure PVP (b) PVP+MgSO4.$7H_2O$+TiO_2 (95:5); (c) PVP+$MgSO_4.7H_2O$+TiO_2 (90:10) (d) PVP+$MgSO_4.7H_2O$+TiO_2 (85:15); (e) PVP+ $MgSO_4.7H_2O$+TiO_2 (80:20)

Composition Studies

The ionic conductivity (σ) as a function of different wt % of MgSO4.7H_2O doped with nano particles was studied. The ionic conductivity of all samples increases with the addition of salt concentration (wt %). Hence it is evident that at higher concentration for (80:20) the conductivity raises rather than the other samples, this may be due to the motion of ions in solid polymer electrolyte is like liquid flow mechanism by which the moment of ions through the polymer matrix is assisted by a large multiples of polymer segmental motion[24].

dc Conductivity Studies

The temperature dependence of dc conductivity of the polymer electrolyte in the temperature range 303-373 K is shown in Fig.-3. The ionic conductivity of pure PVP polymer electrolyte at room temperature is 1.02×10^{-9} Scm^{-1} and the conductivity increased to $1.12 \times 10^{-6} Scm^{-1}$ at 373 K. Whereas for nano particle doped polymer films of 5 %, 10 % 15 % and 20 % the conductivity is found to be 3.06×10^{-5}, 3.78×10^{-5}, 5.59×10^{-5} and 1.21×10^{-4}.

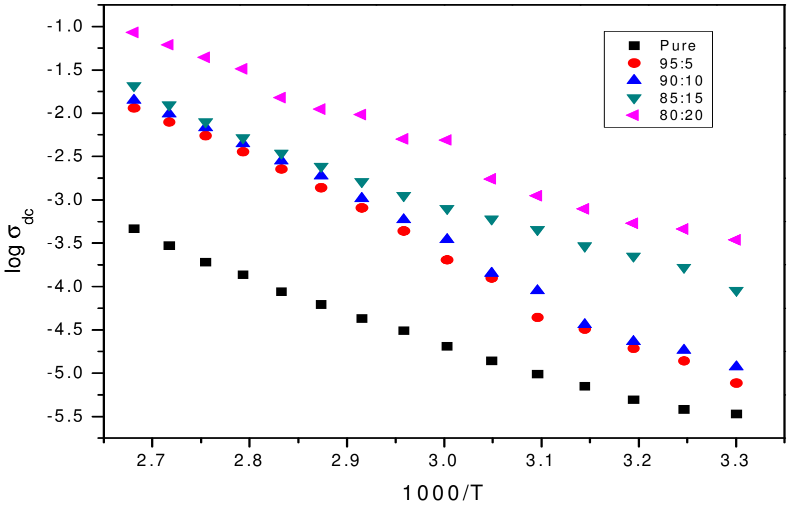

Fig.-3: dc conductivity of (a) Pure PVP (b) (a) Pure PVP; (b) PVP+MgSO4.7H_2O+TiO_2 (95:5) (c) PVP+$MgSO_4$.7H_2O+TiO_2 (90:10); (d) PVP+$MgSO_4$.7H_2O+TiO_2 (85:15); (e) PVP+ $MgSO_4$.7H_2O+TiO_2 (80:20)

The conductivity was calculated by using the relation-

$$\sigma_{dc} = ixl/VxA \text{ (S/cm)} \qquad (1)$$

Where, i is the current, l is the thickness of the film, V is the applied voltage and A is the area of the cross section of the film.

From the obtained values it is noticed that the ionic conductivity is raised of the order 2. This enhancement is due to the increase of doping concentration of TiO_2 nano particles in the polymer films which interacts with either anion or cation thereby reduces the ion pair formation and increases the charge carriers[25]. The activation energy is high for 80:20 concentration further by increasing the salt percentage the activation energy may be decreased. This may be due to the ion segregations which decreases overall mobility.

Transport Properties

The transference number of ionic and electronic (t_{ion} and t_{ele}) was calculated by Wagner's polarization technique. The variation of current as a function of time is measured at constant voltage 2.5 V as shown in Fig.-4. By the application of an external voltage to the circuit a potential is developed and the total current is obtained. Due to the saturation of ions the current starts decreasing with respect to time.

The transference number (t_{ion} and t_{ele}) is calculated by using the equitation's -
$t_{ion} = i_t - i_{ele}/i_t$ and $t_{ele} = i_{ele}/i_t$ (2)

Where, i_t is the initial current and i_{ele} is the final residual current of Solid polymer electrolyte

When a sample is sandwiched between the electrodes the polarization takes place and the ions are blocked at the blocking electrode and the ions get drifted at unblocking electrode. From the plot the values of ionic transference number are measured and they are in the range 0.94-0.98. It results that the charge transport takes place in these polymer films is mainly due to ions, as well as residual of electrons is also takes place.
Mobility of sold polymer electrolyte is measured by using transient ionic current method[26]. The mobility of ions is calculated by using the equation-
$\mu = d^2/TV$ (3)

Where, d is the thickness of the sample, T is the time of flight and V is the applied voltage (2.5 V). The mobility for solid polymer electrolyte is found to be 6.02×10^{-13}(m^2/Vs) for (80:20).

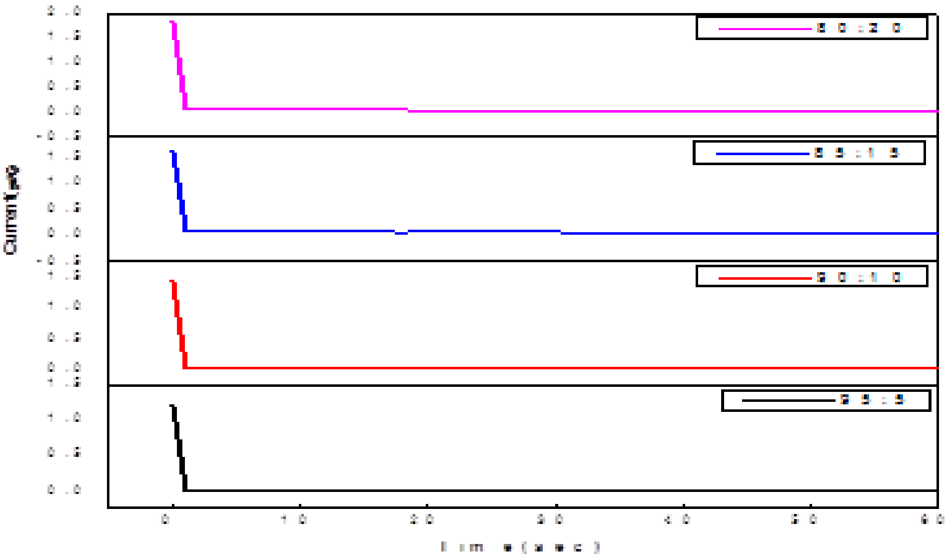

Fig.-4: Transport studies of (a) PVP+MgSO4.7H_2O+TiO_2 (95:5); (b) PVP+$MgSO_4$.7H_2O+TiO_2 (90:10) (c) PVP+$MgSO_4$.7H_2O+TiO_2 (85:15); (d) PVP+ $MgSO_4$.7H_2O+TiO_2 (80:20)

Discharge Characteristics

A Solid state battery has been fabricated with the configuration of Mg (anode)/polymer electrolyte/ (I+C+electrolyte)/ (cathode) at room temperature. The anode and cathode materials were made in the form of a pellet with the thickness of 1mm. In the anode region the charge carrier's takes place due to the magnesium metal and the mixture of iodine and carbon powder is acting as active cathode material which enhances its electronic conductivity. The discharge characteristics were studied for a constant load of 100 kΩ. Initially a rapid decrease in the voltage is occurred; it may be due to the polarization and/or the formation of thin layer of magnesium salt at the electrode/electrolyte interfaces. Fig.5 shows the discharge characteristics of solid state battery having highest conductivity for 80:20 having long durability and exhibits better performance. The cell parameters like open circuit voltage (OCV), short circuit current (SCC), current density and power density etc were calculated and mentioned in the Table-1.

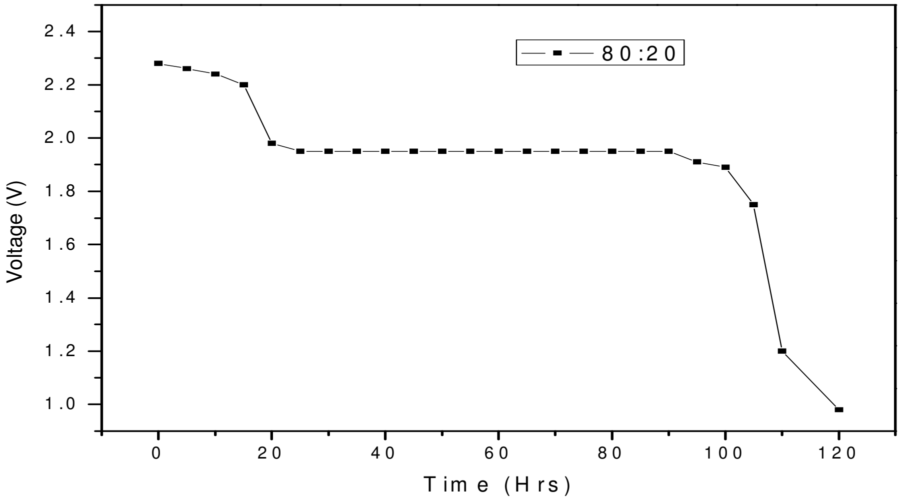

Fig.-5: Discharge characteristics of PVP + $MgSO_4.7H_2O+TiO_2$ (80:20)

Table-1: Cell parameters

Cell parameters	PVP+ $MgSO4.7H_2O$ (80:20)
Cell weight (g)	1.90
Area of the cell (cm^2)	1.45
Current density ($\mu A/cm^2$)	1.13
Open circuit voltage (OCV)	2.25
Discharge time (Hrs)	119
Power density (W/Kg)	1.94
Energy density (Wh/Kg)	231.11
Discharge cell ($\mu A/h$)	13.82

CONCLUSION

XRD concludes that the intensity of the peak is decreased with increasing the salt concentration. FTIR studies showed that the complexation between the salt and polymer. From the conductivity studies the highest conductivity for PVP+ $MgSO4.7H_2O+TiO_2$ (80:20) was found to be 1.21×10^{-4}S/cm at temperature 373 K and the transference of ionic and electronic numbers are found to be in the range 0.94-0.98. This reports that the charge carriers in these polymer electrolyte films are mainly due to ions rather than electrons. By using these polymer electrolyte films a solid state battery has been fabricated and their discharge characteristics were studied.

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