IONIC CONDUCTIVITY AND DISCHARGE STUDIES OF PVP-MgSO₄.7H₂O POLYMER ELECTROLYTE FOR SOLID STATE BATTERY APPLICATIONS

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ABSTRACT

Ionic conducting solid polymer electrolyte films has been prepared with PVP (poly vinyl pyrrolidone) and it is complexed with magnesium sulphate heptahydrate ($MgSO_47H_2O$) by solution casting technique. Different experimental techniques such as FTIR and UV-visible, were used to characterize these polymer electrolytes and electrical, ionic properties of these films were studied by DC conductivity, weight composition, and transport and discharge characteristics. Conductivity measured at the temperature range 303 K to 373 K and it is found that the ionic conductivity of PVP polymer electrolyte is about 7.04×10^{-8} S/cm at room temperature, the highest conductivity is found to be 1.75×10^{-5} S/cm at 373K, for sample with 15% of $MgSO_4.7H_2O$ in PVP polymer. The transference number data reveals that the dominance of ions and charge carriers takes place in this polymer electrolyte system. An electrochemical cells has been fabricated with the configuration of $Mg^+/(PVP + MgSO_4.7H_2O)/(I_2 + C + electrolyte)$ and discharge characteristics were studied under the constant load of 100k Ω. Various cell parameters such as open circuit voltage (OCV), short circuit current (SCC), energy density, and power density has been calculated.

Key words: FTIR, UV-Visible, Polymer electrolytes, Ionic conductivity, Transference number, Electrochemical cell, 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. Armand et al.[3] reported a combination of metal salts gives an electrolyte, with high ionic conductivity, good mechanical strength, high thermal and electrical properties because these solid polymer electrolytes plays an important role and are used in high energy batteries, fuel

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cells, sensors, display devices etc.[4,5] 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[6]. With 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 efforts have been made in developing of new polymer electrolytes having high mechanical, thermal, electrochemical stability and high ionic conductivity[7,8]. These 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. Abdelrazek[9] has reported the physical properties of $MgCl_2$-filled PMMA films for optical applications. Pandey et al.[10] have prepared magnesium ion conducting gel polymer electrolytes dispersed with fumed silica for rechargeable magnesium battery application[10]. Reddy and Chu[11] studied the PEO-Mg polymer electrolyte system. Noto et al.[12] have done a research on Li and Mg polymer electrolytes based on esters of ethylenediaminetetraacetic acid and PEG400.

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 environment 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 on 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 blend electrolytes was prepared based on polyvinyl pyrolidone complexed with $MgSO_4.7H_2O$ by solution casting technique. Various experimental techniques have been used to characterize the films such as conductivity measurements, transport characteristics, mobility and activation energy. Depending on these polymer electrolytes, an electrochemical cell has been fabricated with the configuration of anode/polymer electrolyte/cathode and discharge characteristics of the cell were studied at a constant load of 100 kΩ.

EXPERIMENTAL

Material preparation

PVP of average molecular weight 360,000 from Sigma Aldrich Chemicals was used.

Magnesium sulphatehepta hydrate ($MgSO_4.7H_2O$) (98%, CDH, India) was dried at $50^{\circ}C$ under vacuum for 48 hrs. The double sterilized water was used as common solvent.

Polymer electrolyte preparation

PVP (polyvinylpyrolidone) based solid polymer electrolytes films doped with pure magnesium sulphate heptahydrate were prepared in the different ratios (95:5) (90:10), (85:15) and (80:20) by using solution casting technique using double distilled water as a solvent. Various concentrations of PVP and $MgSO_4.7H_2O$ are mixed thoroughly, the mixture of these solutions was stirred for 48 hours to obtain a homogeneous solution. Later the obtained solution was placed into the polypropylene dishes and evaporated 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.

Characterization

The obtained dried thin films were characterized with FTIR, and UV-Visible spectra. The FTIR spectra were recorded with the help of Perkin Elmer FTIR spectrometer in the range 4000 to 500 cm^{-1}. The complex formation between PVP and $MgSO_4.7H_2O$ has been studied from the FTIR data. The effect of the solvent in the solid polymer electrolyte and optical band gap was measured from the UV-visible studies. The D. C. conductivities of the films were measured at the temperature range 303-373 K. The effect of temperature and salt concentration on the conductivity of PVP was studied with lab made conductivity set up.

The transport properties of ionic and electronic numbers (t_{ion} and t_{ele}) were evaluated by means of Wagner's polarization technique[13], under a DC bias at 2.5V. The resulting current was monitored as a function of time with a Keithley electrometer (Keithley Inc., Model 6514). An electrochemical cell has been fabricated with the configuration of Mg/(PVP + $MgSO_4.7H_2O$)/(I + C + electrolyte) and its discharge characteristics were observed at constant load of 100 KΩ.

RESULTS AND DISCUSSION

FTIR analysis

Fourier transform infrared (FTIR) spectroscopy is used to analyze the chemical structure of polymeric materials, nature of functional group and also to identify the formation of new bonds, and vibrational modes on the polymeric films. In the present study, the FTIR spectra of pure PVP, complexed with $MgSO_4.7H_2O$ with different ratios are shown in Fig. 1.
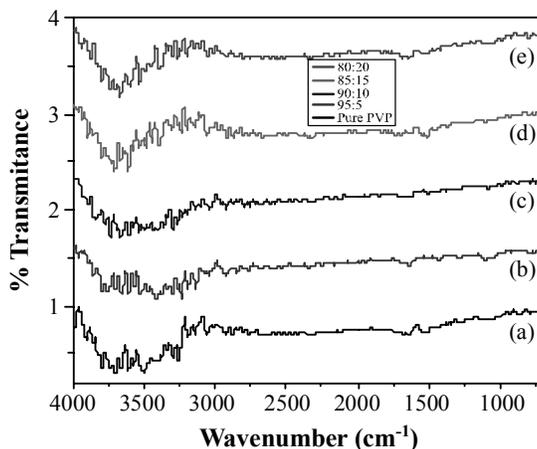
Fig. 1: FTIR analysis (a) Pure PVP (b) PVP + MgSO$_4$.7H$_2$O (95:5)
(c) PVP + MgSO$_4$.7H$_2$O (90:10) (d) PVP + MgSO$_4$.7H$_2$O (85:15)
(e) PVP + MgSO$_4$.7H$_2$O (80:20)

By adding the salt to the host polymer, the complexation takes place with an interaction between salt and the host polymer matrix. This influences the local structure of polymer backbones and significantly affects their mobility. FTIR gives the possible complexation and interaction of ions. PVP complexed with MgSO$_4$.7H$_2$O in various compositions in the wave number range 400-4000 cm^{-1}. The vibrational band is observed at 1500, 3500, 3700, 3800 cm^{-1} are dye to aliphatic C-H stretching, C-H$_2$ bending, CH$_2$ wagging and CN stretching of pure PVP[13,14]. The bands at 1500-1600 cm^{-1} obtained due to C-H stretching, C-H$_2$ bending of PVP, respectively. The band at 3500-3800 cm^{-1} is corresponding to salt completely mixed with the polymer further. It has been observed from the Fig. that the vibrational bands of pure PVP at 1500, 3500 and 3800 cm^{-1} are shifted to lower frequency and some peak intensity decreases with increase in the salt concentration. C-H bending vibrations are between 1500 cm^{-1} to 3800 cm^{-1} while 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 PVP and MgSO$_4$.7H$_2$O salt.

UV-Visible studies

UV-Vis spectroscopy is a versatile technique to investigate the formation of vibrational bonds and their temperature dependence In the ultra-violet region (UV-vis region). The clusters exhibit a characteristics vibrational modes in an energy level. Fig. 2 shows the UV-vis absorption spectra of pure PVP and different ratios of MgSO$_4$.7H$_2$O solid electrolytes at ambient temperatures 373 K. It was absorbed that a hump of an absorption peak was found at the 350-370 nm, which can be attributed to the surface plason bond,

where the electrons are exited from energy level. while no peaks was obtained on increasing the wavelength becomes linear the with the excited transitions of an electron or band to band gap energy takes place as it raises the absorption process
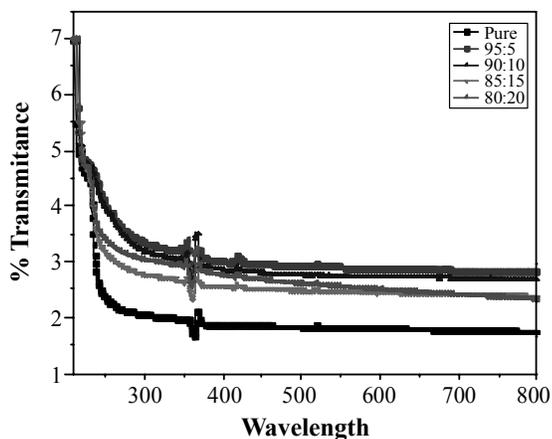

Fig. 2: UV-visible analysis (a) Pure PVP (b) PVP+ MgSO₄.7H₂O (95:5) (c) PVP+ MgSO₄.7H₂O (90:10) (d) PVP+ MgSO₄.7H₂O (85:15) (e) PVP+ MgSO₄.7H₂O (80:20)

DC conductivity studies

The conductivity of pure PVP and its blends with $MgSO_4.7H_2O$ was found to be increasing with temperature and its Wt% of salt are shown in Fig. 3.
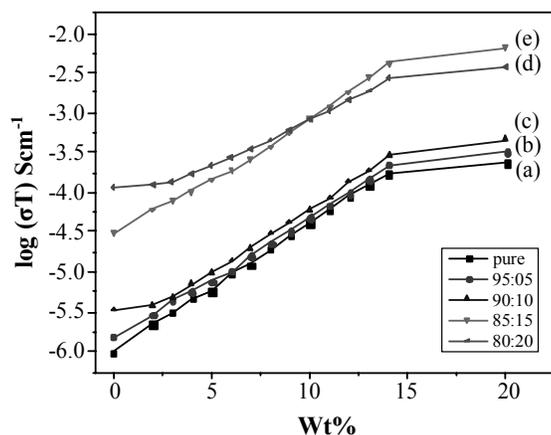

Fig. 3: Composition studies plots of (a) Pure PVP (b) PVP + MgSO₄.7H₂O (95:5) (c) PVP + MgSO₄.7H₂O (90:10) (d) PVP + MgSO₄.7H₂O (85:15) (e) PVP + MgSO₄.7H₂O (80:20)

The data reveals that the conductivity of pure PVP is 1.02×10^{-9} Scm^{-1} at RT and its value increases sharply to 1.12×10^{-6} Scm^{-1} at 373 K and the other salt percentage ratios are found to be 6.40×10^{-7}, 1.75×10^{-5}, 8.74×10^{-7} and 9.7×10^{-6} S/cm with 5%, 10% 15% and 20% with MgSO$_4$.7H$_2$O, respectively. From the values, it is observed that the increase in 1 order in case of pure PVP, where as in case of other blends, it is to be 2 orders. It revealed increase in conductivity by increasing the salt concentration. It was observed that as the temperature was increased the conductivity increases. The conductivity was calculated by –

$$\sigma_{dc} = L/RA \qquad \qquad \dots(1)$$

The increase in conductivity with temperature can be explained by Arrhenius plots, which is having two regions above and below a certain temperature. At a certain temperature lower region i.e. in Region 1, the conductivity of all electrolyte systems increases slowly as the temperature increases. At a desired position, there is a sudden increase in conductivity as is shown in Fig. 4
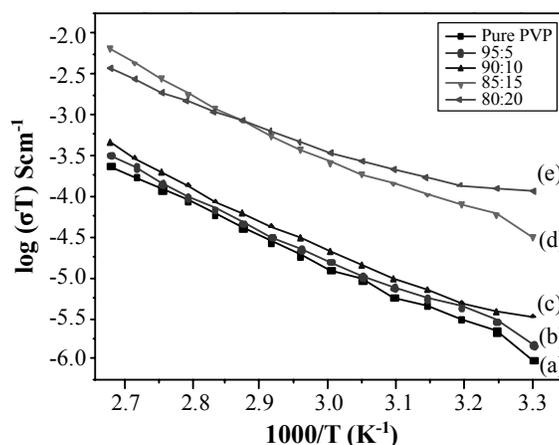

Fig. 4: DC conductivity plots (a) Pure PVP (b) PVP + MgSO$_4$.7H$_2$O (95:5) (c) PVP + MgSO$_4$.7H$_2$O (90:10) (d) PVP + MgSO$_4$.7H$_2$O (85:15 (e) PVP + MgSO$_4$.7H$_2$O (80:20)

However in the region above this temperature i.e. in Region 2, the conductivity again increases slowly with increasing temperature. This change may be attributed to the transition from semi-crystalline phase to amorphous phase[15]. As a result, polymer chain acquires faster internal modes, where bond rotation produces segmental motion. This favors hopping of ions in between the chains. Due to the hopping mechanism between coordinating sides, local structure relaxation and segmental motion of the polymer conductivity in these regions is

given by Arrhenius relation. Therefore, the conductivity becomes high. Fig. 5 indicates the variation of activation energy with varying the $MgSO_4.7H_2O$ concentration. It explains that the activation energy is decreased for the 85:15 of PVP and $MgSO_4.7H_2O$, and as a result, the conductivity is increased.
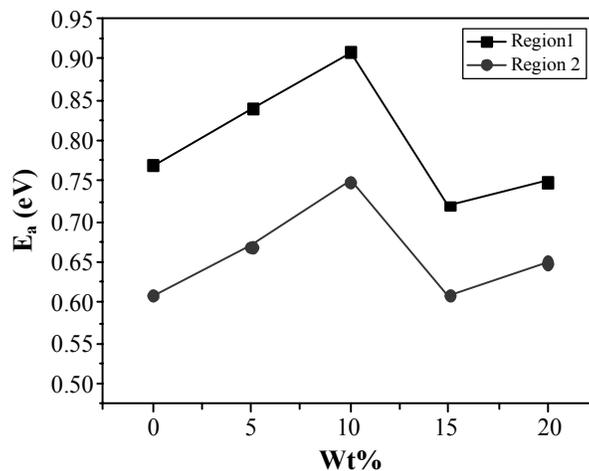

Fig. 5: Activation energy plots (a) Region 1 (b) Region 2

Table 1: Conductivity, activation energies and transference numbers of (PVP + $MgSO_4.7H_2O$) electrolyte system

Films	Conductivity at *RT* (Scm⁻¹)	Conductivity at 373 K (Scm⁻¹)	Activation energies (eV)		Transference number	
			Region 1	Region 2	Tion	Tele
Pure PVP	1.14×10^{-8}	1.23×10^{-6}	0.768	0.603	-	-
PVP + $MgSO_4.7H_2O$ (95:5)	3.2×10^{-9}	6.4×10^{-7}	0.835	0.652	0.93	0.07
PVP + $MgSO_4.7H_2O$ (90:10)	5.09×10^{-8}	8.74×10^{-7}	0.912	0.734	0.95	0.05
PVP + $MgSO_4.7H_2O$ (85:15)	1.29×10^{-7}	1.75×10^{-5}	0.725	0.611	0.97	0.03
PVP+ $MgSO_4.7H_2O$ (80:20)	3.89×10^{-7}	9.70×10^{-6}	0.757	0.652	0.98	0.02

A plot of sigma DC versus 1000/T for pure PVP in the temperature range 30°-100^oC is presented in Fig. 7. The conductivity is found to be 2.62×10^{-6} S/cm.

From Fig. 4, composition studies was observed. As the salt percentage (wt.%) was increased, the conductivity of all samples also increases.

Fig. 5 explains the variation of activation energy with $MgSO_4.7H_2O$ concentration. It was also observed that (PVP+ $MgSO_4.7H_2O$) (85:15) has highest conductivity and lowest activation energy as compared to other samples.

Transference number

Electronic and ionic transference number measurements play an important role in explaining the conductivity of the polymer electrolyte systems. The transference number corresponding to t_{ion} and t_{ele} transport has been calculated and it is shown in Table 3. The transference number of polymer electrolyte system was calculated by Wagner's polarizing technique, while current was noted with respect to time. After polarization of the cell with 2.5 volts dc, the current vs time plots were obtained (Fig. 6).
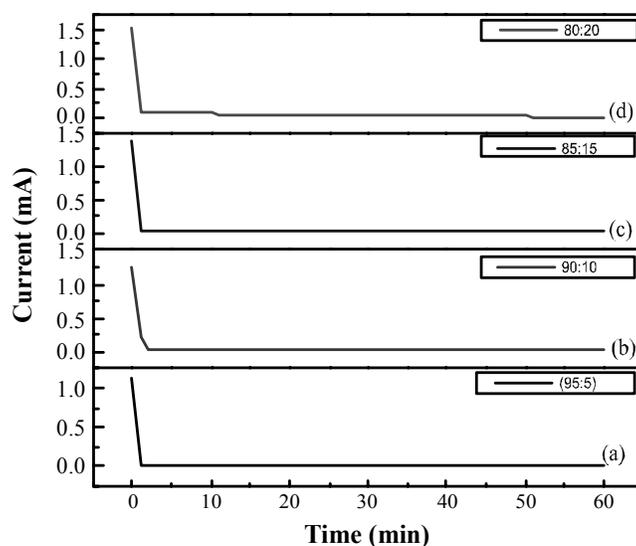

**Fig. 6: Transport characteristics plot (a) Pure PVP (b) PVP + MgSO₄.7H₂O (95:5)
(c) PVP + MgSO₄.7H₂O (90:10) (d) PVP + MgSO₄7H₂O (85:15)
(e) PVP + MgSO₄.7H₂O (80:20)**

As the transference number of all samples is close to unity, here the charge transport takes place due to the potassium ions, while the charge transport (t_{ele}) is very small.

Table 2: Transference number and mobility of solid polymer electrolytes

Electrolytes	Transference number (t_{ion})	Mobility (μ) (m^2/Vs)
Pure PVA	-	0.95×10^{-8}
PVP + MgSO$_4$.7H$_2$O (95:5)	0.93	3.11×10^{-8}
PVP + MgSO$_4$.7H$_2$O (90:10)	0.95	3.25×10^{-8}
PVP + MgSO$_4$.7H$_2$O (85:15)	0.97	3.56×10^{-8}
PVP + MgSO$_4$.7H$_2$O (80:20)	0.98	3.98×10^{-8}

The transference number (t_{ion} and t_{ele}) are calculated from the polarization current versus time plots using the equation –

$$t_{ion} = i_t - i_{ele}/i_t \quad \text{and} \quad t_{ele} = i_{ele}/i_t \qquad \text{…(2)}$$

Where i_t is the initial current and i_{ele} is the final residual current for all compositions of PVP + MgSO$_4$.7H$_2$O

The values of ionic transference number are in the range 0.94-0.98 for electrolyte systems. The charge transport in these polymer films is mainly due to ions, as well as minor transfer of electrons also takes place. Mobility of the ionic species (Mg^{2+}) are measured using transient ionic current method[16]. The mobility of ions in SPE is determined using the equation.

$$\mu = d^2/TV \qquad \text{…(3)}$$

Where d is the thickness of the sample, T is the time of flight and V is the applied voltage (2.5 V). The calculated mobility was found to be $2.98 \times 10^{-8} m^2/Vs$ at (80:20) for PVP + MgSO$_4$.7H$_2$O.

Discharge characteristics

Solid state electrochemical cells were fabricated using Mg (anode)/polymer electrolyte/(I + C + electrolyte)/(cathode) for different compositions, and the thickness of the electrodes is nearly 1 mm. Here, the potassium metal is used as anode while a mixture of I + C + electrolyte is used as cathode. The anode material and cathode was made in the form of a pellet. In the anode, the charge transfer takes place due to potassium and in cathode, the carbon powder material enhances its electronic conductivity[16]. Their discharge characteristics were studied for a constant load of 100 kΩ at room temperature.
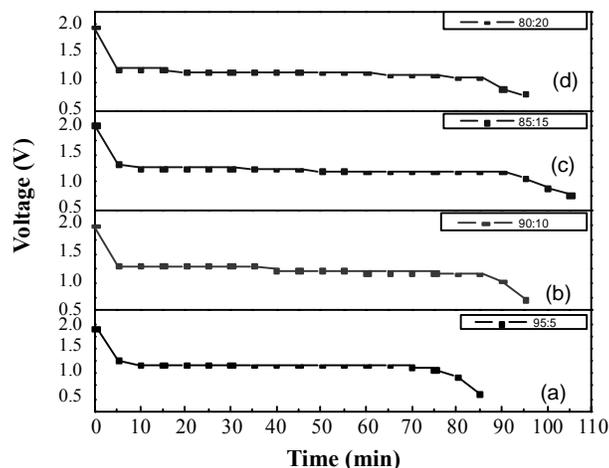
Fig. 7: Discharge characteristics plots (a) Pure PVP (b) PVP + MgSO₄.7H₂O (95:5)
(c) PVP + MgSO₄.7H₂O (90:10) (d) PVP + MgSO₄.7H₂O (85:15)
(e) PVP + MgSO₄.7H₂O (80:20)

Fig. 7 shows the discharge profiles of the electrochemical cells of various compositions. The initial sharp decrease in the voltage for all the cells may be due to the polarization and formation of a thin layer of potassium salt at the electrode-electrolyte interface[18-32].

Table 3: Cell parameters of Mg/[MgSO₄.7H₂O]/(I₂ + C + electrolyte)

Cell parameters	PVA + MgSO₄.7H₂O (95:5)	PVA + MgSO₄.7H₂O (90:10)	PVA + MgSO₄.7H₂O (85:15)	PVA + MgSO₄.7H₂O (80:20)
Cell weight (g)	1.31	1.31	1.31	1.31
Area of the cell (cm²)	1.42	1.42	1.42	1.4
Open circuit voltage (OCV)	1.8	1.87	2.0	1.9
Discharge time (Hrs)	87	98	108	95
Current density (mA/cm²)	0.84	0.83	0.82	0.81
Discharge cell (mA/h)	13.7	12.2	11.1	12.6
Power density (W/Kg)	1.64	1.58	1.69	1.60
Energy density (W h/Kg)	142.68	154.84	182.52	152

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 4. It is clear that the cell with the composition (PVP+ $MgSO_4.7H_2O$) (80:20) exhibits better performance and stability than other compositions[18].

Table 4: Cell parameters of polymer electrolyte batteries

Solid state electro chemical cell	Open circuit voltage (OCV)	(V) Discharge time for plateau region (Hrs)	Reference
Na/(PVA + NaF)/(I$_2$ + C + electrolyte)	2.53	112	28
Mg/(PVA+ Mg(CH$_3$COO)$_2$)/(I$_2$ + C+ electrolyte)	1.84	87	16
Mg/(PEO +Mg(NO$_3$)$_2$)/(I$_2$ + C + electrolyte)	1.85	142	3
K/(PVP+PVA+KClO$_3$)/(I$_2$ + C + electrolyte)	2.00	52	29
K/(PVP + PVA + KBrO$_3$)/(I$_2$ + C + electrolyte)	2.30	72	30
Mg/(PEG + Mg(CH$_3$COO)$_2$)/(I$_2$+ C +electrolyte)	1.84	32	31
Ag/(PEO + AgNO$_3$)/(I$_2$ + C + electrolyte)	0.595	48	32
K/(PVA + CH$_3$COOK)/(I2 + C + electrolyte)	2.0	75	10
Mg/[MgSO$_4$.7H$_2$O]/(I$_2$ + C + electrolyte)	2.0	108	Present

These cell parameters demonstrate potential applications of these polymer electrolytes in solid state electrochemical cells

CONCLUSION

FTIR studies indicate that there complexation between the salt and polymer. The highest conductivity for PVP+ $MgSO_47H_2O$ (85:15) was found to be 1.75×10^{-5} S/cm at temperature 373 K. Transference of ionic and electronic numbers were found to be in the range 0.93-0.98. This suggests that the charge carriers in these polymer electrolyte films are mainly due to ions rather than electrons. The electrochemical cell using polymer electrolyte films has been fabricated and their discharge characteristics were studied.

ACKNOWLEDGEMENT

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