

PREPARATION AND CHARACTERIZATION OF PVA BASED SOLID POLYMER ELECTROLYTES FOR ELECTROCHEMICAL CELL APPLICATIONS

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Abstract Solid polymer electrolyte films containing poly(vinyl alcohol) (PVA) and magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) were prepared by solution casting technique and characterized by using XRD, FTIR, DSC and AC impedance spectroscopic analysis. The amorphous nature of the polymer electrolyte films has been confirmed by XRD. The complex formation between PVA and Mg salt has been confirmed by FTIR. The glass transition temperature decreases with increasing the Mg salt concentration. The AC impedance studies are performed to evaluate the ionic conductivity of the polymer electrolyte films in the range of 303–383 K, and the temperature dependence seems to obey the Arrhenius behavior. Transport number measurements show that the charge transport is mainly due to ions. Electrochemical cell of configuration $\text{Mg}/(\text{PVA} + \text{Mg}(\text{NO}_3)_2) (70:30)/(\text{I}_2 + \text{C} + \text{electrolyte})$ has been fabricated. The discharge characteristics of the cell were studied for a constant load of 100 k Ω .

Keywords: Polymer electrolyte; XRD; DSC; Ionic conductivity; Electrochemical cell.

INTRODUCTION

In the recent years, there has been a tremendous interest in the preparation of polymer electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities because these polymer electrolytes play a major role in solid-state batteries, electrochromic windows, sensors, fuel cells *etc*^[1, 2]. These materials consist of alkali metal salt complexes of solid polar polymer, such as poly(ethylene oxide) (PEO)^[3, 4], poly(ethylene glycol) (PEG)^[5], poly(propylene oxide) (PPO)^[6] *etc*. Among them the polymer electrolytes based on PVA have attracted many researchers due to their good electrical and mechanical properties. Most of the commercial poly(vinyl alcohol) samples have been prepared by hydrolyzing the poly(vinyl acetate). Due to the presence of hydroxyl groups, the interchain hydrogen bond of PVA has been developed. This causes the high melting point and good mechanical stability of PVA. Yang and Pavani reported the alkaline PVA based polymer electrolytes for electrochemical cell applications^[7, 8]. But the literature survey reveals that the PVA complexes with magnesium salts are rare.

Lot of exploratory research has been made on monovalent salt systems like Li salts^[9–12]; little attention has been given to the polymer electrolytes in which multivalent cations are the mobile species. Magnesium metal possesses a number of characteristics, which make it attractive as a negative electrode material for rechargeable batteries, such as low cost, relative abundance, high safety, ease of handling and low toxicity which allows for urban waste disposal^[13]. In view of negligible hazards and enhanced safety, studies on rechargeable magnesium batteries are expected to have a wide scope in the future^[13–15]. The present work aims at developing a new type of Mg^{2+} ion conducting polymer electrolyte with PVA as the host. Very few reports are available on magnesium

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salts as dopant^[5, 16–19], hence an attempt has been made to synthesis of PVA based polymer electrolyte with magnesium nitrate as salt. The resultant electrolyte films have been characterized by XRD, FTIR and DSC analyses. The conductivity of the polymer electrolytes has been measured using AC impedance technique in the temperature range of 303–383 K.

EXPERIMENTAL

The solid polymer electrolyte films of PVA and magnesium nitrate doped PVA, PVA:Mg(NO₃)₂, were prepared by weight percent ratios (90:10), (80:20), (70:30) and (60:40) by solution cast technique using triple distilled water as solvent. PVA (molecular weight of 125000) was used as the polymer. Mg(NO₃)₂ was added accordingly. The mixture of these solutions was stirred for 12 h to obtain a homogeneous solution. The solution was then poured into polypropylene dishes and evaporated slowly at room temperature under vacuum. The polymer electrolyte films were then transferred into a desiccator for further drying before the test.

In order to investigate the nature of these polymer electrolyte films, WAXD patterns were recorded in the diffraction angular range $2\theta = 10^\circ$ – 60° by a Philips X'Pert PRO (Almelo, The Netherlands) diffractometer, working in the reflection geometry and equipped with a graphite monochromator on the diffracted beam (CuK α radiation). The thermal response was studied by differential scanning calorimetry (TA Instruments mod. 2920 calorimeter) in the static nitrogen atmosphere at a heating rate of 5 K/min. in the temperature range of 0 °C to 140 °C. Impedance measurements were carried out in the temperature range 303–383 K using HIOKI 3532-50 LCR Hitester over a frequency range from 42 Hz to 5 MHz. The transference number measurements were made using Wagner's polarization technique^[20]. Solid-state electrochemical cells were fabricated in the configuration Mg/(PVA + Mg(NO₃)₂)/(I₂ + C + electrolyte). The discharge characteristics of the cells were monitored under a constant load of 100 k Ω .

RESULTS AND DISCUSSION

XRD and FTIR Studies

Figure 1 represents the XRD patterns of pure PVA, pure Mg(NO₃)₂ and different compositions of PVA-Mg(NO₃)₂ polymer electrolytes. The mechanism of ionic transport in polymer electrolytes is still not completely understood, but there is a significant motion of polymer chains existing in the amorphous domain or phase while non-conducting in the crystalline phase. The XRD pattern of PVA solid polymer electrolyte film shows a broad peak between 17° and 22° , which is associated with the amorphous domain of PVA polymer matrix. This peak

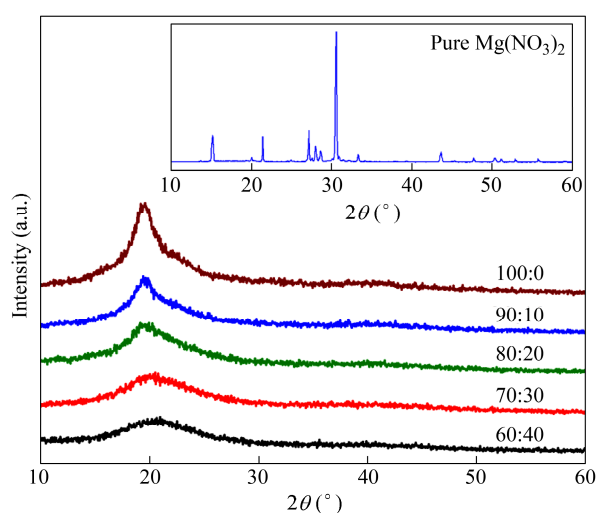


Fig. 1 X-ray diffraction patterns of pure Mg(NO₃)₂ and PVA:Mg(NO₃)₂ complexes

corresponds to (110) reflection. The PVA matrix combined with $\text{Mg}(\text{NO}_3)_2$ has a larger domain of amorphous phase, so the ionic conductivity of polymer electrolyte can be significantly enhanced. No peaks pertaining to magnesium nitrate salt appeared in XRD patterns of the complexes, which indicated the complete dissolution of magnesium salt in the polymer matrices. The XRD studies confirmed the fact that there exists a definite complex coordination between PVA and magnesium nitrate salt.

FTIR spectroscopy has been used to analyze the interactions among atoms or ions in electrolyte systems. These interactions can induce changes in the vibrational modes of the polymer electrolyte. The FTIR spectra of pure PVA, pure $\text{Mg}(\text{NO}_3)_2$ and PVA: $\text{Mg}(\text{NO}_3)_2$ (70:30) are shown in Figs. 2(a)–2(c).

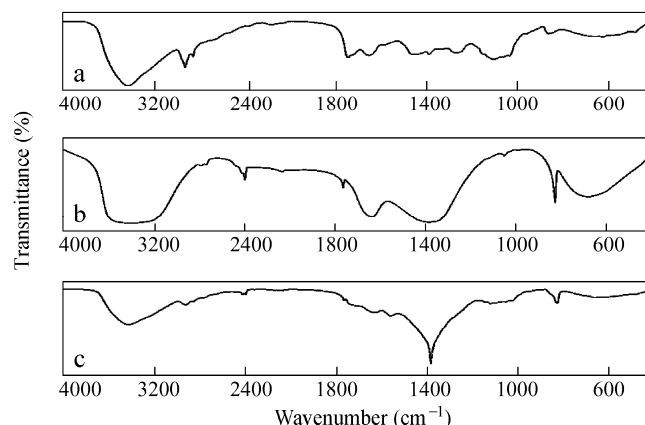


Fig. 2 FTIR spectra of (a) pure PVA, (b) pure $\text{Mg}(\text{NO}_3)_2$ and (c) PVA: $\text{Mg}(\text{NO}_3)_2$ (70:30)

The absorption peak at 853 cm^{-1} has been assigned to C—H rocking of pure PVA^[19] (Fig. 2a). This peak is shifted to 833 cm^{-1} in 30 wt% $\text{Mg}(\text{NO}_3)_2$ doped polymer electrolyte system (Fig. 2c). The band at about 1098 cm^{-1} corresponds to C—O stretching of acetyl groups present on the PVA backbone. This peak is shifted to 1122 cm^{-1} in the complexed system (Fig. 2c). CH_2 bending observed in pure PVA at 1452 cm^{-1} is found to be shifted to higher wave numbers in the complexed system. A broad and strong peak centered at 3436 cm^{-1} which could be assigned to the stretching vibration of hydroxyl groups (ν_{OH}) with strong hydrogen bonding of intra and inter types of pure PVA is shifted in the complexed system. The C=O stretching at 1736 cm^{-1} of pure PVA^[21] is found to be shifted to higher wave numbers in the complexed system. For instance in the case of 30 wt% $\text{Mg}(\text{NO}_3)_2$ doped PVA, the C=O peak is shifted from 1736 cm^{-1} to 1764 cm^{-1} . This clearly shows that the interaction between the salt and PVA not only arises from O—H groups but also from C—O groups of pure PVA. The broad peak around 2925 cm^{-1} corresponds to the asymmetric C—H stretching of pure PVA. This peak is found to be shifted in the salt-doped system. The group frequencies at 667, 826, 1384 and 2397 cm^{-1} of $\text{Mg}(\text{NO}_3)_2$ are found in the polymer complex. Hence from FTIR spectroscopy the interaction between PVA and $\text{Mg}(\text{NO}_3)_2$ and their complex formation have been confirmed.

DSC Studies

Figure 3 is the DSC thermograms of pure PVA and $\text{Mg}(\text{NO}_3)_2$ doped PVA solid polymer electrolyte films. From Fig. 3, the glass transition temperature T_g of PVA is about 85°C , which was reported by Mohamad^[22]. The addition of magnesium nitrate can reduce T_g of the host polymer significantly. The low glass transition temperature is observed for 30 wt% $\text{Mg}(\text{NO}_3)_2$ doped PVA polymer electrolyte which is about 76.04°C . It can be attributed to a great effect of magnesium nitrate on softening of the complexation due to the plasticizing effect of the guest salt on the polymer structure, which is beneficial for the magnesium ion transport in the anhydrous membrane. The glass transition temperature values are given in Table 1.

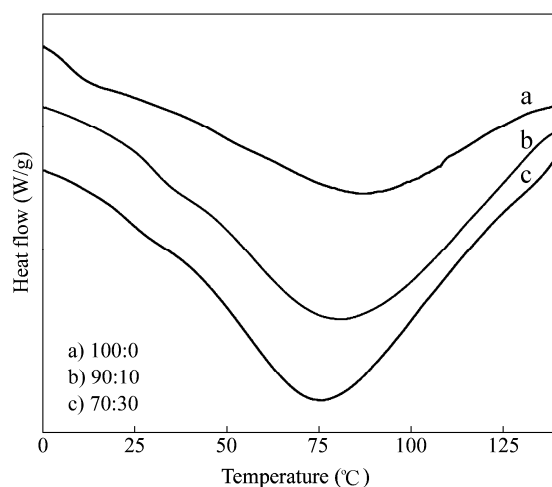


Fig. 3 DSC curves of PVA:Mg(NO₃)₂ SPEs: (a) 100:0, (b) 90:10 and (c) 70:30

Table 1. T_g values of PVA:Mg(NO₃)₂ polymer electrolyte films

S. No	Sample	T_g (°C)
1	Pure PVA	85
2	90:10	78.67
3	70:30	76.04

Conductivity Studies

The ionic conductivity of polymer electrolytes as a function of magnesium nitrate concentration at room temperature is shown in Fig. 4. The results indicate that the room temperature conductivity of PVA is about 5.9×10^{-9} S/cm^[16] and increases sharply with increase in magnesium salt content. The high ionic conductivity in an electrolyte is attributed to the increased ionic mobility and ionic charge carrier concentration. The enhancement of ionic conductivity increases with increasing salt concentration and the maximum value at 30 wt% of Mg(NO₃)₂ is 7.36×10^{-7} S/cm. Clearly the decrease in conductivity at high salt concentration is due to decrease in free ions due to formation of ion-ion pairing. This trend is similar to the results reported by various researchers in studies on various polymer electrolyte systems using the concept of ion association and formation of charge multiplets^[23–25].

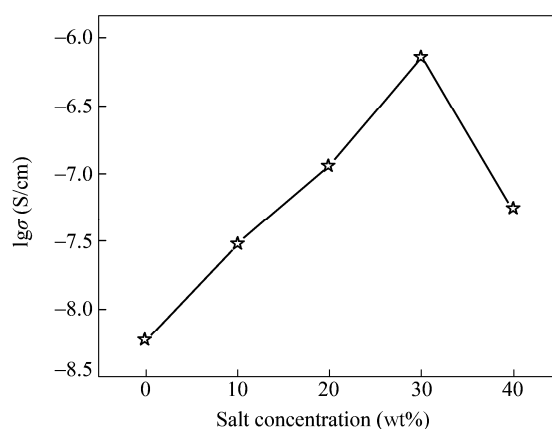


Fig. 4 Effect of the concentration of magnesium nitrate on the conductivity of polyvinyl alcohol at room temperature (303 K)

The logarithmic conductivity as a function of frequency for PVA:Mg(NO₃)₂ electrolytes with different compositions at 303 K and that for the 70PVA:30Mg(NO₃)₂ polymer complex at different temperatures are shown in Figs. 5(a) and 5(b) respectively. As seen in the figures, the frequency-dependent conductivity plots show two distinct regions. The first region observed at low frequencies corresponds to the frequency-independent conductivity. This conductivity value has been assigned to the bulk conductivity of the sample (σ_{dc}). In the high-frequency region, the conductivity increases with increasing frequency. The σ_{dc} value has been calculated from the extrapolation of the plateau region to the Y-axis. The maximum conductivity was found to be 7.32×10^{-7} S/cm at 303 K for the 70PVA:30Mg(NO₃)₂ polymer electrolyte. The dc conductivity values obtained from conductance spectra have been found to coincide with the bulk conductivity values obtained from the impedance plot. From Fig. 5(b), it has been found that the dc conductivity increases with increase of temperature which suggests that the free volume around the polymer chain causes the increase in mobility of ions, polymer segments and hence the conductivity.

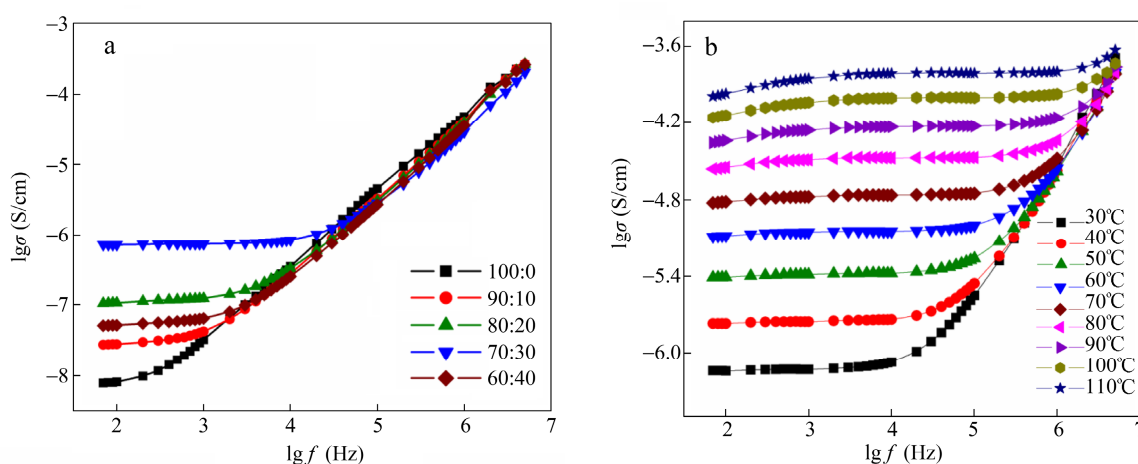


Fig. 5 Conductance spectra of (a) PVA:Mg(NO₃)₂ with different salt concentrations at 303 K and (b) 70PVA:30Mg(NO₃)₂ polymer electrolyte at different temperatures

In general, it is believed that the conductivity increases as the degree of crystallinity decreases or, in other words, the flexibility of the polymeric backbone increases. The crystalline regions obstruct ion movement by blocking the paths of the ions, but the increase of amorphous region is due to an increase in free volume. The increase in free volume would facilitate the motion of ionic charges, *i.e.*, the migration of ions through the amorphous region. The increase of conductivity in this PVA system with the increase of salt is attributed to a decrease in the degree of crystallinity and dominant presence of amorphous region.

Figure 6 shows the temperature dependent conductivity of the polymer electrolytes with the best ionic conductivity in each system studied through impedance measurements for the temperature ranging from 303 K to 383 K. From Fig. 6, it can be seen that the polymer electrolytes show the Arrhenius behavior as the ionic conductivity enhanced almost linearly with the increment of temperature. The activation energy values were calculated from Fig. 6 using the following Arrhenius equation: $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 is a constant, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. The activation energy values were 0.72, 0.73, 0.77, 0.67 and 0.76 eV for pure and 10%, 20%, 30% and 40% Mg(NO₃)₂ complexed PVA films, respectively. The activation energy does not show any significant change in these systems. Miyamoto and Shibayama^[26] explained that ionic conductivity increased with increasing temperature as a result of the free volume model. According to that model, as the temperature increases, the polymer electrolyte can expand easily and produce free volume. Therefore, ions, solvated molecules, or the polymer segments can move into the free volume, causing its increase^[27]. This enhances the ion and polymer segmental mobility that will, in turn, enhance the ionic conductivity. The ionic conductivity values at different temperatures are given in Table 2.

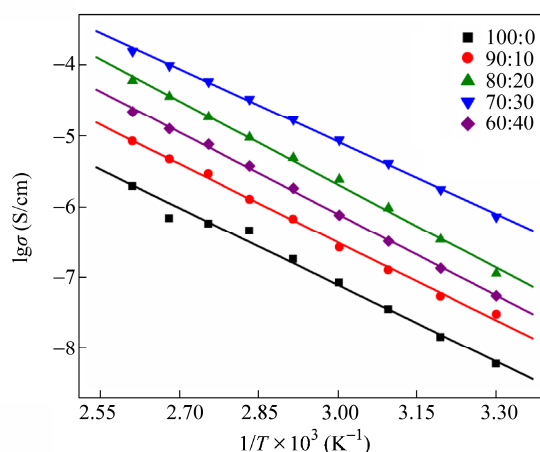


Fig. 6 Temperature dependent conductivity of PVA:Mg(NO₃)₂ polymer electrolytes

Table 2. Ionic conductivity values of PVA:Mg(NO₃)₂ polymer electrolyte films at different temperatures

Sample	Ionic conductivity × 10 ⁷ (S/cm)								
	303 K	313 K	323 K	333 K	343 K	353 K	363 K	373 K	383 K
100:0	0.059	0.143	0.352	0.84	1.83	4.6	5.79	6.96	19.6
90:10	0.302	0.545	1.28	2.71	6.76	12.8	29.3	47.5	85
80:20	1.14	3.47	9.79	24.4	48.8	95.4	186	360	605
70:30	7.36	17.6	40.8	88	171	333	588	992	1570
60:40	0.555	1.36	3.27	7.72	18.4	37.6	76.2	127	223

Transference Number

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transports have been calculated for 70PVA:30Mg(NO₃)₂ polymer electrolyte film using Wagner's DC polarization technique^[20]. In this method, the DC current is monitored as a function of time on the application of a fixed DC voltage across the Mg/(PVA + Mg(NO₃)₂) (70:30)/C cell. After applying 1.5 V, the current versus time plot can be obtained, which is shown in Fig. 7 for a (PVA + Mg(NO₃)₂) (70:30) electrolyte. The transference number has been calculated from the polarization current versus time plot using the equation: $t_{\text{ion}} = (I_i - I_f)/I_i$, where I_i is the initial current and I_f is the final residual current. The ionic transference number (t_{ion}) for 70PVA:30Mg(NO₃)₂ polymer electrolyte system is found to be *ca.* 0.98. This suggests that the charge transport in this electrolyte film is predominantly due to ions.

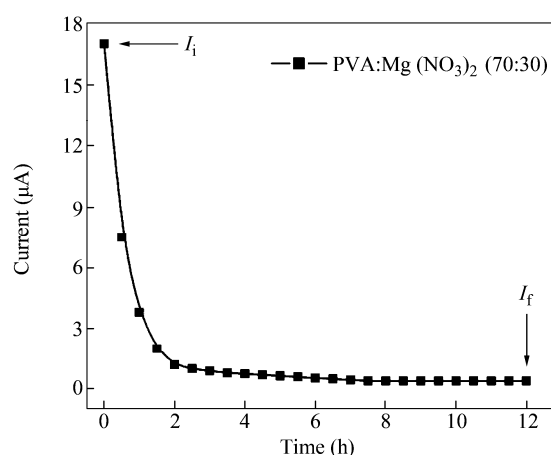


Fig. 7 Polarization current versus time plot of (PVA + Mg(NO₃)₂) (70:30) electrolyte film

Battery Discharge Studies

Figure 8 shows the discharge characteristics of the electrochemical cell Mg/(PVA + Mg(NO₃)₂)/(I₂ + C + electrolyte) for a constant load of 100 kΩ. The initial sharp decrease in the voltage of these cells may be due to polarization and/or the formation of a thin layer of magnesium salt at the electrode-electrolyte interface. The cell parameters for this cell were evaluated, and they are listed in Table 3. The results of the present investigation are comparable with the results of earlier workers as depicted in Table 4. This suggests a possible application of the present polymer electrolyte in solid state batteries.

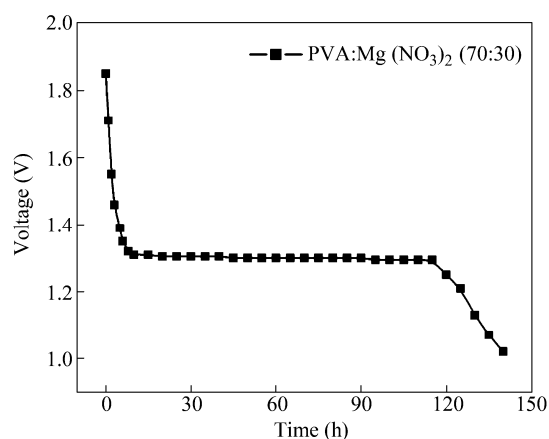


Fig. 8 Discharge characteristic plot of (PVA + Mg(NO₃)₂) (70:30) electrochemical cell for a constant load of 100 kΩ

Table 3. Cell parameters of (PVA+ Mg(NO₃)₂) electrolyte cell for a constant load of 100 kΩ

Cell parameters	Mg/(PVA + Mg(NO ₃) ₂) (70:30)/(I ₂ + C + electrolyte)
Cell weight	1.472 g
Area of the cell	1.33 cm ²
Open circuit voltage (OCV)	1.85 V
Discharge time for plateau region	105 h
Current density	13.91 μA/cm ²
Discharge capacity	1.943 mA h
Power density	16.34 mW/kg
Energy density	2.288 W h/kg

Table 4. Comparison of present cell parameters with the data of other cells reported earlier

Solid state electrochemical cell configuration	Open circuit voltage (OCV) (V)	Discharge time for plateau region (h)	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	82	[31]
Ag/(PEO + AgNO ₃)/(I ₂ + C + electrolyte)	0.595	48	[32]
Mg/(PVA + Mg(NO ₃) ₂)/(I ₂ + C + electrolyte)	1.85	105	Present

CONCLUSIONS

The polymer electrolytes PVA-Mg(NO₃)₂ with different compositions have been prepared by solution cast technique. The amorphous nature and polymer-salt complex formation were confirmed by the XRD and FTIR studies. The DSC measurements showed a decrease in the degree of crystallinity and increase of amorphous

regions with increasing concentration of salt. The highest conductivity observed is of the order of 7.36×10^{-7} S/cm for the 70PVA:30Mg(NO₃)₂ polymer electrolyte at 303 K. The temperature dependence of ionic conductivity reveals the Arrhenius type thermally activated process. The ionic transport number data in the PVA + Mg(NO₃)₂ polymeric electrolyte films indicate that the conduction is predominantly due to ions rather than electrons. Using (PVA + Mg(NO₃)₂) (70:30) electrolyte, electrochemical cell has been fabricated for which the open-circuit voltage is 1.85 V. The cell parameters evaluated for the present cell is comparable with the cell parameters of earlier reported cells, thus offering an interesting option of application of these electrolytes for solid state batteries.

REFERENCES

- 1 Vincent, C. and Scrosati, B., "Modern batteries: an introduction to electrochemical power sources", John Wiley and Sons, Inc, New York, 1997
- 2 Guhan, S., Arun Kumar, N. and Sangeetha, D., Chinese J. Polym. Sci., 2009, 27(2): 157
- 3 Ramalingaiah, S., Srinivas Reddy, D., Jaipal Reddy, M., Laxmi Narasaiah, E. and Subba Rao, U.V., Mater. Lett., 1996, 29: 285
- 4 Al-Hawarin, J., Ayesha, A.S. and Abdel-Rahem, R.A., Chinese J. Polym. Sci., 2012, 30(2): 143
- 5 Polu, A.R., Kumar, R., Causin, V. and Neppalli, R., J. Korean Phy. Soc., 2011, 59: 114
- 6 Carlsson, P., Swenson, J., McGreevy, R.L., Gabrys, B., Howells, W.S., Börjesson, L. and Torell, L.M., Physica B: Condensed Matter, 1997, 234-236: 231
- 7 Yang, C.C., Lin, S.J. and Wu, G.M., Mater. Chem. Phys., 2005, 92: 251
- 8 Pavani, Y., Ravi, M., Bhavani, S., Sharma, A.K. and Rao, V.V.R.N., Polym. Eng. & Sci., 2012, 52: 1685
- 9 Every, H.A., Zhou, F., Forsyth, M. and MacFarlane, D.R., Electrochim. Acta, 1998, 43: 1465
- 10 Rajendran, S., Sivakumar, M. and Subadevi, R., Solid State Ionics, 2004, 167: 335
- 11 Malathi, J., Kumaravadivel, M., Brahmanandhan, G.M., Hema, M., Baskaran, R., and Selvasekarapandian, S., J. Non-cryst. Solids, 2010, 356: 2277
- 12 Chatterjee, J., Liu, T., Wang, B. and Zheng, J.P., Solid State Ionics, 2010, 181: 531
- 13 Gregory, T.D., Hoffman, R. J. and Winterton, R.C., J. Electrochem. Soc., 1990, 137: 775
- 14 Novak, P., Imhof, R. and Haas, O., Electrochim. Acta, 1999, 45: 351
- 15 Aurbach, D., Lu, Z., Schechter, A., Gofer, Y., Gizbar, H., Turgeman, R., Cohen, Y., Moshkovich, M. and Levi, E., Nature, 2000, 407: 724
- 16 Polu, A.R. and Kumar, R., Int. J. Polym. Mater., 2013, 62: 76
- 17 Jeong, S.K., Jo, Y.K. and Jo, N.J., Electrochim. Acta, 2006, 52: 1549
- 18 Jaipal Reddy, M. and Chu, P.P., Solid State Ionics, 2002, 149: 115
- 19 Liebenow, C., Electrochim. Acta, 1998, 43: 1253
- 20 Wagner, J.B. and Wagner, C.J., Chem. Phys., 1957, 26: 1597
- 21 Karthikeyan, K., Vinatier, P. and Levasseur, A., Bull. Mater. Sci., 2000, 23: 179
- 22 Wu, G.M., Lin, S.J. and Yang, C.C., J. Membr. Sci., 2006, 275: 127
- 23 Singh, T.J. and Bhat, S.V., Bull. Mater. Sci., 2003, 26: 707
- 24 Hema, M., Selvasekerapandian, S. and Hirankumar, G., Ionics, 2007, 13: 483
- 25 Hirankumar, G., Selvasekerapandian, S., Bhuvaneswari, M.S., Baskaran, R. and Vijaykumar, M., Ionics, 2004, 10: 135.
- 26 Miyamoto, T. and Shibayama, K., J. Appl. Phys., 1973, 44: 5372
- 27 Shriver, D.F. and Ratner, M.A., Chem. Rev., 1988, 88: 109
- 28 Balaji Bhargav, P., Madhu Mohan, V., Sharma, A.K. and Rao, V.V.R.N., Curr. Appl. Phys., 2009, 9: 165
- 29 Subba Reddy, Ch.V., Sharma, A.K. and Narasimha Rao, V.V.R., J. Power Sources, 2002, 111: 357
- 30 Subba Reddy, Ch.V., Sharma, A.K. and Narasimha Rao, V.V.R., Polymer, 2006, 47: 1318
- 31 Polu, A.R. and Kumar, R., E-J. Chem., 2012, 9: 869
- 32 Rao, S.S., Rao, K.V.S., Shareefuddin, Md., Subba Rao, U.V. and Chandra, S., Solid State Ionics, 1994, 67: 331