ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Ionic Conductivity and Electrochemical Studies of Mg^{2+} - Ion Conducting PEG-Al_2O_3 Composite Polymer Electrolytes.

Anji Reddy Polu*

Materials Physics Division, School of Advanced Sciences, VIT University, Vellore, TN, India 632014

ABSTRACT

Composite polymer electrolyte materials are very attractive for components of batteries and opto-electronic devices. PEG-$Mg(NO_3)_2$ polymer electrolytes and their composites were prepared by using addition of different wt. % of Al_2O_3 ceramic fillers. Several experimental techniques, such as composition-dependence conductivity, temperature dependence conductivity in the temperature range of 303-333 K and transport number measurements, have been employed to characterize these polymer electrolytes. The magnitude of conductivity increased with increase in the concentration of the Al_2O_3 ceramic filler and temperature. The highest ionic conductivity achieved was 3.4×10^{-5} S/cm for the sample prepared with 15 wt % of Al_2O_3 at room temperature. The charge transport in the present composite polymer electrolytes is mainly due to ions. Using these (PEG-$Mg(NO_3)_2$) polymer electrolyte and (PEG-$Mg(NO_3)_2$-Al_2O_3) composite polymer electrolyte, solid-state electrochemical cells were fabricated and their discharge profiles were studied.

Keywords: Composite polymer electrolyte; Ionic conductivity; Transference number; Electrochemical cell.

**Corresponding author*

INTRODUCTION

In the field of polymer electrolytes, interest began after the pioneering studies on polyethylene oxide (PEO) based complexes reported by Wright et.al. [1], Armand and co-workers [2-3]. Solid polymer electrolytes i.e., polymer salt complexes, are of technologies interest due to their possible applications as solid electrolytes in various electrochemical devices such as energy conversion units (batteries / fuel cells), electro chromic display devices and photo electrochemical solar cells, etc. [4-5]. Among the electrochemical devices, polymer electrolytes have been widely studied and developed for battery applications over the past three decades. Composite polymer electrolytes (CPEs) comprising of a polymer host, doping salt and inorganic / ceramic filler were first demonstrated by Weston and Steele in 1982 [6]. The addition of fillers into the polymer matrixes improves both the mechanical strength of the polymer [6-7] and their ionic conductivities [8]. The additives used include SiO_2 [9], ZrO_2 [10], TiO_2 [11], CeO_2 [12], Al_2O_3 [13] etc., and in most work on composite polymer electrolytes, the electrolyte is usually based on high molecular weight PEO [7-8]. Little attention has been paid to the somewhat low molecular weight polymers.

Many types of solid polymer electrolytes (SPEs) have been proposed based on organic polymer matrixes which dissolved inorganic salts, especially such alkali metal salts [14-15]. Contrarily, little has been published for materials in which multivalent (divalent, trivalent, or tetravalent) cations are the mobile species [16-17]. Indeed, materials showing Mg^{2+} conductivity are quite interesting due to the following advantages: 1. The ionic radii of Li^+ and Mg^{2+} are 68 and 65 pm, respectively, i.e., comparable in magnitude. Hence, easy replacement of Li^+ ions by Mg^{2+} ions in insertion compounds is possible. 2. Magnesium metal is more stable than the lithium. It can be handled safely in oxygen and humid atmospheres unlike lithium which requires high purity argon or helium atmosphere. Therefore, safety problems associated with magnesium metal are minimal. 3. Global raw material resources of magnesium are plentiful and thus, it is much cheaper than the lithium [18]. Bearing these facts in mind, we have prepared poly (ethylene glycol) (PEG) of molecular weight 4000, complexed with $Mg(NO_3)_2$ salt.

In present paper, we report the PEG-$Mg(NO_3)_2$ solid polymer electrolytes and composite polymer electrolytes prepared by the addition of Al_2O_3 particles to PEG-$Mg(NO_3)_2$ (85-15). The purpose of this work is to emphasis the extraordinary effect occurring in the PEG-$Mg(NO_3)_2$-Al_2O_3 composite polymer electrolytes. Our results demonstrate that the dispersion of Al_2O_3 particles in the PEG-$Mg(NO_3)_2$ matrix leads to an increase in the ionic conductivity of the CPEs. The conductivity of the CPEs are measured using ac impedance technique in the temperature range 303-333 K.

EXPERIMENTAL

PEG (average molecular weight 4,000) purchased from CDH, India, was dried at 40°C for 5 h; $Mg(NO_3)_2$ (CDH, India) was dried at 40°C for 24 h, and Al_2O_3 (< 50 nm) procured from Sigma Aldrich, was used. Solid polymer electrolyte samples were prepared using the solution cast technique. PEG (molecular weight of 4,000) was used as the polymer. $Mg(NO_3)_2$ was added accordingly. The solvent used in this work is distilled water. The mixture was stirred up to 10 hours to obtain a homogeneous solution. After incorporating the required amount of Al_2O_3 ceramic particles was suspended in the solution and stirred for about 10 h. The solution was then poured into the glass petri dishes and evaporated slowly at room temperature under vacuum. The polymer electrolyte samples were then transferred into desiccators for further drying before the test.

When the polymer electrolyte films have formed they were placed between the blocking stainless steel electrodes of the conductivity cell with leads connected to a HIOKI 3532-50 LCR meter interfaced to a computer for conductivity measurements. The measurements were made over a frequency range of 42Hz to 5MHz at different temperatures. The temperature dependent conductivity studies were carried out for PEG-$Mg(NO_3)_2$- x wt. % of Al_2O_3 (x = 0, 5, 10, 15 and 20) composite polymer electrolyte films. Conductivity measurements were carried out over the same frequency range for temperatures ranging from room temperature to 333 K. The conductivity cell with connecting lead wires were placed in an oven with temperature control facilities. The transference number measurements were made using Wagner's polarization technique [19]. Solid-state electrochemical cells were fabricated in the configuration Mg/(PEG-$Mg(NO_3)_2$)/(I_2+C+electrolyte) and Mg/(PEG-$Mg(NO_3)_2$-Al_2O_3)/(I_2+C+electrolyte). The discharge characteristics of the cells were monitored under a constant load of 100 kΩ.

RESULTS AND DISCUSSION

Conductivity Studies

The ionic conductivity of solid polymer electrolytes as a function of magnesium nitrate concentration at room temperature (303 K) is shown in Fig. 1. Pure PEG shows a low ionic conductivity ($\sigma = 5.41 \times 10^{-8}$ S/cm) at room temperature (303 K). With the addition of 15 wt. % of $Mg(NO_3)_2$ salt, the ionic conductivity enhanced to 3.34×10^{-6} S/cm. The conductivity increases initially with the increasing salt concentration as the number of charge carriers increases, but at higher salt concentration, the conductivity decreases because of the increasing influence of the ion pairs, ion triplets, and the higher ion aggregations, which reduces the overall mobility and the number of effective charge carriers.

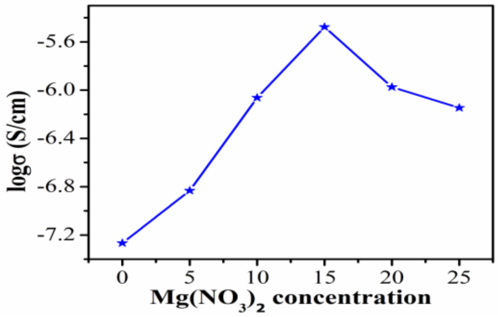

Fig 1: Effect of the concentration of magnesium nitrate on the conductivity of PEG at room temperature (303 K)

The effect of filler content on the ionic conductivity of the 85PEG-15Mg$(NO_3)_2$ with Al_2O_3 at five different contents 0, 5, 10, 15 and 20 wt. % was examined. The filler content dependence on ionic conductivity in the CPEs at room temperature is shown in Fig. 2. The ionic conductivity of the CPE increased with an increase in filler content and reached a maximum value, then started decreasing with further addition of filler. The highest conductivity 3.40 x 10^{-5} S/cm was obtained at the Al_2O_3 content of 15 wt %. The room temperature conductivity values are given in Table 1. The increase in conductivity has been attributed to: (i) the ceramic particles acting as nucleation centers for the formation of minute crystallites [20]; (ii) the ceramic particles aiding in the formation of amorphous phase in the polymer electrolyte [21]; (iii) the formation of the new kinetic path via polymer–ceramic boundaries [22]. However, the conductivity is found to decrease after an optimum concentration of Al_2O_3 is crossed. As the optimum concentration is attained, on further addition of filler a continuous non-conductive phase build up by large amount of fillers as an electrically inert component would block up Mg-ion transport, resulting in an increase in total resistance of the composite polymer electrolyte.

Table 1: Ionic conductivity values of PEG-Mg$(NO_3)_2$ and PEG-Mg$(NO_3)_2$-Al_2O_3 compositions at room temperature (303 K).

PEG-Mg$(NO_3)_2$ composition	Ionic conductivity σ (S/cm)	PEG-Mg$(NO_3)_2$-Al_2O_3 composition	Ionic conductivity σ (S/cm)
100:0	5.41 x 10^{-8}	85:15:00	3.34 x 10^{-6}
95:05	1.47 x 10^{-7}	85:15:05	6.82 x 10^{-6}
90:10	8.65 x 10^{-7}	85:15:10	1.12 x 10^{-5}
85:15	3.34 x 10^{-6}	85:15:15	3.40 x 10^{-5}
80:20	1.06 x 10^{-6}	85:15:20	2.06 x 10^{-5}
75:25	7.14 x 10^{-7}		

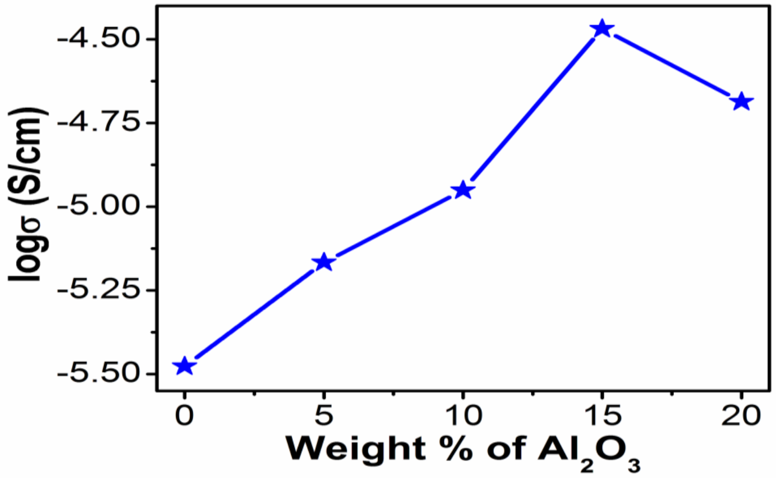

Fig 2: Effect of the concentration of Al_2O_3 on the conductivity of 85PEG-15Mg$(NO_3)_2$ polymer electrolyte at room temperature (303 K).

The temperature dependence of ionic conductivity of PEG-Mg$(NO_3)_2$- x wt. % of Al_2O_3 (x = 0, 5, 10, 15 and 20) composite polymer electrolytes are shown in Fig. 3. The curvature shown in these plots indicates that the ionic conduction obeys the VTF relation which describes the transport properties in a viscous matrix [23-25]. It is found that as temperature increases, the conductivity values also increase for all the compositions. As the temperature increases, the polymer can expand easily and produce free volume. Thus ions, solvated molecules or polymer segments may move in to the free volume. The resulting conductivity is represented by overall mobility of ion and polymer which is determined by the free volume around polymer chain. The increase in free volume leads to the increase in ion mobility and segmental mobility that will assist the ion transport.

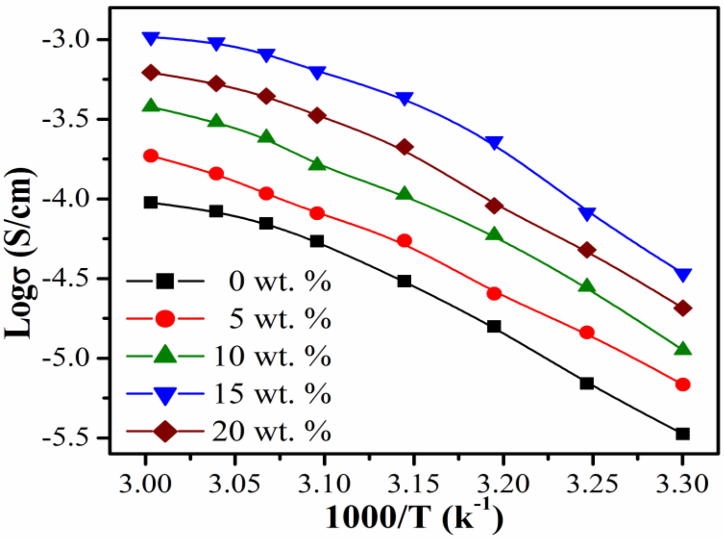

Fig 3: Temperature dependent conductivity of 85PEG-15Mg(NO_3)$_2$- x wt. % of Al_2O_3 (x = 0, 5, 10, 15 and 20) composite polymer electrolytes.

Transference Number Studies

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport have been calculated for (PEG-Mg(NO_3)$_2$-Al_2O_3) (85-15-15) CPE film using wagner's dc polarization technique [19]. In this method, the dc current is monitored as a function of time on the application of fixed dc voltage across the Mg/(PEG-Mg(NO_3)$_2$-Al_2O_3) (85-15-15)/C cell. After applying 1.5 V, the current versus time plot was obtained, which is shown in Fig. 4 for a (PEG-Mg(NO_3)$_2$-Al_2O_3) (85-15-15) electrolyte. The transference number has been calculated from the polarization current versus time plot using the equation

$$t_{ion} = \frac{(I_i - I_f)}{I_i} \qquad (1)$$

where I_i is the initial current and I_f is the final residual current. The ionic transference number (t_{ion}) for (PEG-Mg(NO_3)$_2$-Al_2O_3) (85-15-15) CPE system is found to be ~0.98. This suggests that the charge transport in this electrolyte film is predominantly due to ions.

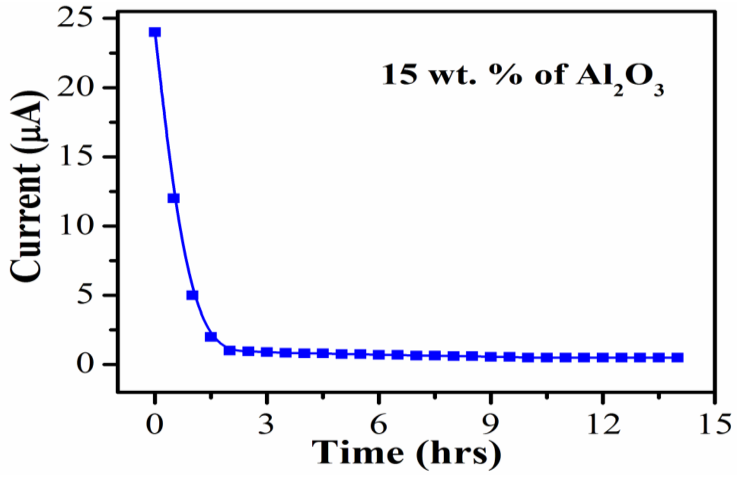

Fig 4: Polarization current vs. time plot of (PEG-$Mg(NO_3)_2$-Al_2O_3) (85-15-15) electrolyte film.

Battery Discharge Studies

The discharge characteristics of the cells Mg/(PEG-$Mg(NO_3)_2$) (85-15)/(I_2+C+electrolyte) and Mg/(PEG-$Mg(NO_3)_2$-Al_2O_3) (85-15-15)/(I_2+C+electrolyte) at an ambient temperature for a constant load of 100 kΩ are shown in Fig. 5 (a-b). The initial sharp decrease in voltage of these cells may be due to polarization and/or formation of a thin layer of magnesium salt at the electrode-electrolyte interface. Various cell parameters obtained for both the cells are shown in Table 2. The cell parameters for a number of solid state cells reported earlier are given in Table 3 along with the data of present cells. From the Table 3, it is clear that the cell parameters of the present electrolyte systems are comparable with the cell parameters reported for other cells, thus offering an interesting option of application of these electrolytes for solid state batteries.

Table 2: Cell parameters of (PEG-$Mg(NO_3)_2$) (85-15) and (PEG-$Mg(NO_3)_2$-Al_2O_3) (85-15-15) polymer electrolyte cells for a constant load of 100 kΩ.

Cell parameters	Mg/(PEG-$Mg(NO_3)_2$)(85:15)/ (I_2+C+electrolyte)	Mg/(PEG-$Mg(NO_3)_2$-Al_2O_3)(85:15:15)/ (I_2+C+electrolyte)
Cell weight	1.83 g	1.84 g
Area of the cell	1.33 cm^2	1.33 cm^2
Open Circuit Voltage (OCV)	1.80 V	1.85 V
Discharge time for plateau region	84 h	102 h
Current density	13.53 $\mu A/cm^2$	13.91 $\mu A/cm^2$
Discharge capacity	1.512 m A h	1.887 m A h
Power density	12.49 m W/Kg	13.47 m W/Kg
Energy density	1.624 W h/Kg	2.021 W h/Kg

Table 3: Comparison of present cells 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
Ag/(PVP-$AgNO_3$)/(I_2+C+electrolyte)	0.46	82	[26]
Mg/(PVA-$Mg(NO_3)_2$)/(I_2+C+electrolyte)	1.85	105	[27]
Na/(PEO-NaYF4)/(I_2+C+electrolyte)	2.45	96	[28]
Mg/(PEO-$Mg(NO_3)_2$)/(I_2+C+electrolyte)	1.85	142	[29]
Mg/(PEG-$Mg(CH_3COO)_2$)/(I_2+C+electrolyte)	1.84	82	[30]
Mg/(PVA-$Mg(CH_3COO)_2$)/(I_2+C+electrolyte)	1.84	87	[31]
Mg/(PVA-PEG-$Mg(NO_3)_2$)/(I_2+C+electrolyte)	1.85	120	[32]
Mg/(PEG-$Mg(NO_3)_2$)/(I_2+C+electrolyte)	1.80	84	Present
Mg/(PEG-$Mg(NO_3)_2$-Al_2O_3)/(I_2+C+electrolyte)	1.85	102	Present

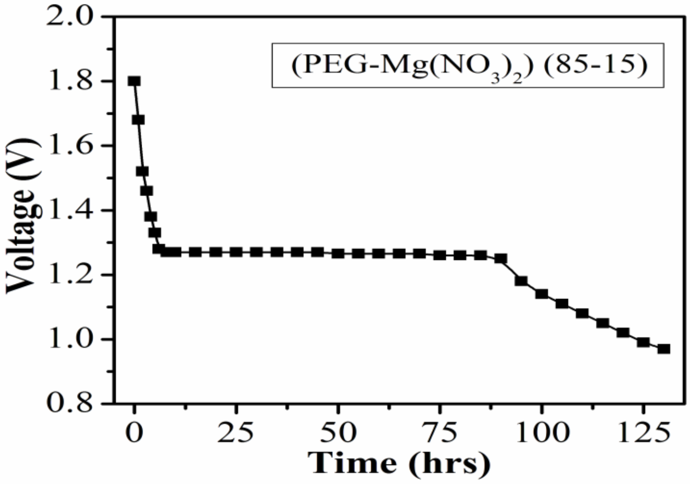

Fig 5a: Discharge characteristic plot of (PEG-$Mg(NO_3)_2$) (85-15) electrochemical cell for a constant load of 100 kΩ.

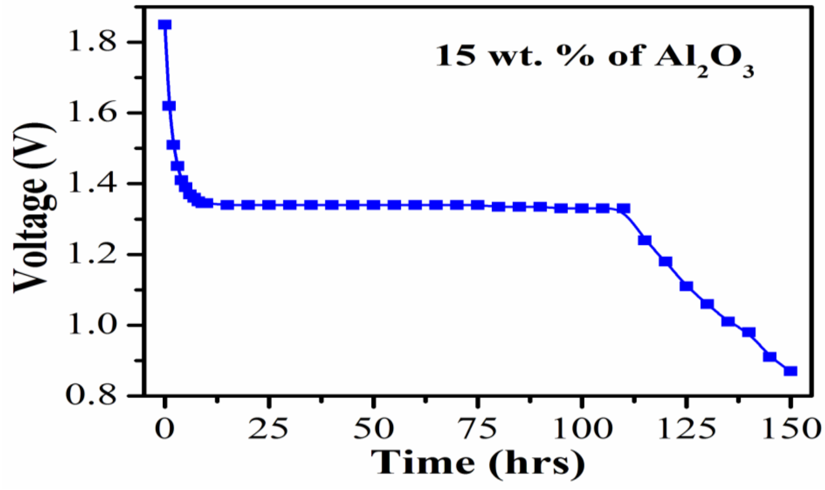

Fig 5b: Discharge characteristic plot of (PEG-$Mg(NO_3)_2$-Al_2O_3) (85-15-15) electrochemical cell for a constant load of 100 kΩ.

CONCLUSIONS

On the basis of experimental investigations on PEG-$Mg(NO_3)_2$-Al_2O_3 polymer electrolytes, the following conclusions are drawn

1. Using the impedance spectroscopy, the bulk electrical conductivity has been determined. It is found that the conductivity increases and then dips with the addition of Al_2O_3.
2. The maximum value of conductivity obtained is 3.40×10^{-5} S/cm for sample with a 15 wt. % of Al_2O_3 to 85PEG-15$Mg(NO_3)_2$ polymer electrolyte system.
3. The temperature dependent conductivity of composite polymer electrolytes obeys the VTF behavior.
4. The ionic transport number data in the PEG-$Mg(NO_3)_2$-Al_2O_3 polymeric electrolyte films indicate that the conduction is predominantly due to ions.
5. Using (PEG-$Mg(NO_3)_2$) (85-15) and (PEG-$Mg(NO_3)_2$-Al_2O_3) (85-15-15) polymer electrolytes, electrochemical cells were fabricated and the discharge characteristics were studied. Among these cells (PEG-$Mg(NO_3)_2$-Al_2O_3) (85-15-15) was found to be more stable than the other cell.

REFERENCES

[1] Wright PV. Brit Polym J 1975; 7: 319-327.

[2] Armand MB, Chabagno JM, Duclot MJ. in Fast Ion transport in Solids, ed. by Vashista P, Mundy JN, Shenoy GK. Elsevier Applied Science Publishers Ltd., North Holland, Amsterdam, 1979, P 131.

[3] Hasmi SA, Chandra A, Chandra S. in Solid State Ionics: Materials and Applications, ed. by Chowdari BVR. World Scientific, Singapore, 1992, P 567.

[4] Mac Callum JR. in Polymer Electrolyte Reviews, ed. By Vincent CA. Elsevier, Amsterdam, 1987.

[5] Owen JR. in Super Ionic Solids and Solid Electrolytes-Recent trends, ed. By Lasker AL, Chandra S. Academic Press, New York, 1989;P 111.

[6] Weston JE, Steele BCH. Solid State Ionics 1982; 7: 75-79.

[7] Cho J, Liu M. Electrochimica Acta 1997; 42: 1481-1488.

[8] Croce F, Scrosati B. J Power Sources 1993; 43: 9-19.

[9] Chandra A, Chandra A, Thakur K. Indian J Pure & Appl Phys 2013; 51: 44-48.

[10] Rajendran S, Uma T. Mater Lett 2000; 44: 208-214.

[11] Polu AR, Kumar R. E-J Chem 2011; 8: 347-353.

[12] Vijaya kumar G, Karthick SN, Sathiya Priya AR, Ramalingam S, Subramania A. J Solid State Electrochem 2008; 12: 1135-1141.

[13] Polu AR, Kumar R. Adv Mat Lett 2013; 4: 543-547.

[14] Chandra A, Chandra A, Thakur K. Chinese J Polym Sci 2013; 31: 302-308.

[15] Chandra A, Chinese J Polym Sci 2013; 31: 1538-1545.

[16] Polu AR, Kumar R, Joshi GM. Ionics 2013; DOI: 10.1007/s11581-013-1024-9.

[17] Adachi GY. J Mater Chem 2000; 10: 1431-1435.

[18] Munichandraiah N, Girish Kumar G. J Power Sources 2000; 91: 157-160.
[19] Wagner JB, Wagner CJ. Chem Phys 1957; 26: 1597-1601.
[20] Chandra A, Srivastava PC, Chandra S. J Mater Sci 1995; 30: 3633-3638.
[21] Munichandraiah N, Scanlon LG, Marsh RA, Kumar B, Sircar AK. J Appl Electrochem 1995; 25: 857-863.
[22] Przyluski J, Siekierski M, Wieczorek W. Electrochim Acta 1995; 40: 2101-2108.
[23] Vogel H. Phys Z 1922; 22: 645-646.
[24] Tamman VG, Hesse HZ. Anorg Allg Chem 1926; 156: 245-257.
[25] Fulcher GS. J Ame Ceram Soc 1925; 8: 339-355.
[26] Jaipal Reddy M, Sreepathi Rao S, Laxmi Narasaiah E, Subba Rao UV. Solid State Ionics 1995; 80: 93-98.
[27] Polu AR, Kumar R. Chinese J Polym Sci 2013; 31: 641-648.
[28] Sreepathi Rao S, Jaipal Reddy M, Laxmi Narasaiah E, Subba Rao UV. Mater Sci & Eng. B 1995; 33: 173-177.
[29] Ramalingaiah S, Srinivas Reddy D, Jaipal Reddy M, Laxmi Narasaiah E, Subba Rao UV. Mater Lett 1996; 29: 285-289.
[30] Polu AR, Kumar R. E-J Chem 2012; 9: 869-874.
[31] Polu AR, Kumar R. Int J Polym Mater 2013; 62: 76-80.
[32] Polu AR, Kumar R, Dehariya H. AIP Conf Proc 2012; 1447: 969-970.