

Effect of Plasticizer on a new (PEO + NaHCO₃) Solid Polymer electrolyte system for Battery characterization studies

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Abstract

Poly Ethylene Oxide (PEO) - based Solid polymer electrolyte films with NaHCO₃ and NaHCO₃ + plasticizer (Dimethyl formamide) have been Prepared using Solution cast technique. Several experimental techniques such as XRD, IR, and composition dependence conductivity, temperature dependence conductivity in the temperature range of 303- 373K and transport number measurements were employed to characterize this polymer electrolyte system. The complexation of the Polymer PEO with NaHCO₃ and NaHCO₃ + DMF (Dimethyl formamide) was confirmed by XRD and IR studies. The conductivity-temperature plots showed an increasing in conductivity with increasing temperature. The increase in conductivity is about ten times larger in the plasticized-added (PEO + NaHCO₃) polymer electrolyte systems compared with pure (PEO + NaHCO₃) polymer electrolyte system. The transference data indicated that the charge transport in these polymer electrolyte systems is predominantly due to Na⁺ ions. Using this polymer electrolyte system a Polymer battery or an electrochemical cell with configuration Na / (PEO + NaHCO₃ + plasticized) / (I₂ + C + Electrolyte) was fabricated and its discharge characteristics are studied for a constant load of 100 KΩ. The open circuit voltage (OCV), short circuit current (SCC), discharge time etc., were evaluated. A number of other battery parameters associated with the battery were evaluated and compared with the data from earlier reported in this paper.

Keywords: Plasticizer effect, ionic conductivity, polymer electrolyte, transports number, battery characterization.

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1. Introduction

The production, storage and distribution of energy are the main concerns of modern industry and society. Over the past ten years a spectacular development has been seen in microelectronic industry but, to date, the application to integrable power sources has not been still realized. The development of new type of electrical power generators and storage systems are quite essential for the further integration of the electronic industry. The self-contained power source is a growing trend in numerous fields such as pocket calculators, bio-medical devices, cameras and watches. The presently available conventional battery system contains a liquid electrolyte, generally a concentrated aqueous solution of potassium hydride or sulphuric acid. This liquid electrolyte has high ionic conductivity and offers very good contact with electrodes. But the major problems associated with liquid electrolyte are cell leakage, corrosion, self-discharge process, drying out of the cell, loss of electrolyte and severe restrictions on the capability of useful discharge at very low temperatures. Interest in developing solid state batteries was motivated

impart by the hope that the above problems would be minimized when the liquid electrolyte is replaced by a solid electrolyte.

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)[25], electro chromic display devices and photoelectrochemical solar cells, etc., [4,5]. Subsequently, the studies in this field have been reported by PEO based polymer electrolyte complexes using alkali salts [6,7,8]. Some studies on silver ion conducting polymer electrolytes are reported based on PEO [9,10]. The ionic conductivity of a polymer electrolyte with modified carbonate (MC) as a plasticizer in a PEO – LiCF₃SO₃ complex has been studied by Lee et al [11] and Yang et al [12]. The temperature dependence of the conductivity and thermal analysis of PEO – LiCF₃SO₃ with plasticizer (MC)

polymer electrolyte showed an increase in conductivity through the entire complex system.

In the Present Paper, the authors reported solid polymer electrolyte films of PEO, PEO + NaHCO₃ and PEO + NaHCO₃ + Plasticizer (DMF) systems. Plasticizer (DMF) is added to a PEO + NaHCO₃ electrolyte system to study the effect of the plasticizer. Several experimental techniques, such as composition dependent conductivity, temperature dependent conductivity in the temperature ranges 303-373K and transport number measurements were performed to characterize these polymer electrolyte systems. Based on these electrolytes, a solid polymer battery was fabricated with the configuration anode/polymer electrolyte/cathode. The discharge characteristics of the battery have been studied for a constant load of 100 KΩ. The results of these investigations are reported in the present paper.

2. Experimental

Thin Films (thickness \approx 100 - 150 μ m) of pure PEO (Aldrich Mw \approx 6x10⁵) and various compositions of complexed films of PEO with NaHCO₃ salt and PEO with NaHCO₃ + DMF were prepared with different weight ratios (90:10), (80:20), (70:30) by a solution-cast technique using methanol (water free) as solvent. The X-ray diffraction studies of these films are carried out with the help of PHILIPS PW 3710 X-ray diffractometer in the range 10⁰-70⁰. The infrared (IR) spectrum in these films has been recorded with the help of JASCO IT/IR-5300 spectrophotometer in the range 400-4000 cm⁻¹. The dc conductivity has been measured using the lab made conductivity setup [10] in the temperature range 303-373K. The ionic and electronic transport numbers (t_{ion} and t_{ele}) were evaluated by means of Wagner's polarization technique [11, 12]. In this technique, a freshly prepared film of PEO + NaHCO₃ + DMF under a dc bias (step potential 1.5V) was used. The resulting current was monitored as a function of time with a Keithley electrometer (Keithley Inc., model 614). The transient ionic current (TIC) measurement technique [13] is used to evaluate the mobility of the ion species.

A Solid Polymer battery was fabricated with the configuration Na⁺/(PEO + NaHCO₃ + DMF)/(I₂ + C + electrolyte). The details about the fabrication of the electrochemical cells are given elsewhere [14]. The discharge characteristic studies of these electrochemical cells were monitored at a constant load of 100 KΩ.

3. Results and Discussion

The complexed of the polymer PEO, PEO complexed with NaHCO₃ and salt NaHCO₃ were confirmed by using IR spectroscopy. The IR spectra of pure PEO, PEO complexed with NaHCO₃ were recorded with the help of JASCO FT/IR-5300 spectrophotometer in the range 400-4000 cm⁻¹ and are shown in Fig. 1. The intensity of aliphatic C-H stretching vibration band observed around 2950 cm⁻¹ in PEO is observed to be decreases by increasing the concentration of NaHCO₃ salt in the polymer. Also the appearance of new peaks along with changes in existing peaks (and/or their disappearance) in the IR spectra directly indicates the complexation of PEO with NaHCO₃ and

(PEO + NaHCO₃) with plasticizer (DMF). Fig. 2 shows the X-ray diffractogram of PEO + NaHCO₃ and PEO + NaHCO₃ + Plasticizer electrolyte systems. Well-defined sharp peaks are observed indicating the crystalline nature. Thus the result of X-ray diffraction, IR data clearly establish the complexation of NaHCO₃ and plasticizer with different weight ratios with the polymer Poly Ethylene Oxide (PEO). The variation in dc conductivity (σ) as a function of NaHCO₃ + plasticizer composition in PEO at various temperatures is given in Fig. 3. The conductivity data at room temperature is reported in Table 1. From Fig. 3, Table 1 the following conclusions can be drawn.

- In the temperature range of study, the conductivity is found to increases with temperature in pure PEO and also in all the compositions of PEO + NaHCO₃ + plasticizer polymer electrolyte systems.
- The conductivity – temperature plots follow the Arrhenius behavior throughout, but with two regions (region-I and region-II), with two activation energies above and below melting point (T_m) of the polymer. In region-I (i.e. below T_m) the conductivity slowly increases with temperature up to 65⁰C. At 65⁰C there is a sudden increase in conductivity. In the region-II (i.e above T_m) the conductivity again rapidly increases with temperature. Similar behavior has been observed in all the compositions of PEO + NaHCO₃ and PEO + NaHCO₃ + plasticizer polymer electrolyte systems.
- The temperature T_m which corresponds to the melting point (\approx 65⁰C) of the polymer, there is a change from the semi crystalline to amorphous phase transition. Due to phase change, the conductivity shows a sudden increase at T_m . The existence of two regions in the conductivity – temperature plots has been observed in a number of PEO based polymer electrolytes [15-17]. The conductivity of pure PEO is about 6.78 x 10⁻¹⁰ Scm⁻¹ at room temperature (R_T) and its value increases with relative concentration of NaHCO₃. The magnitude of change is of the order of 10³ times in PEO + NaHCO₃ (90: 100), (80: 20) and 10⁴ times in PEO + NaHCO₃ + plasticizer (90: 10), (80: 20) electrolyte systems, respectively compared to that of pure PEO polymer.
- The conductivity data plots of log (σT) versus ($10^3 / T$) for (PEO + NaHCO₃), (PEO +NaHCO₃ + Plasticizer) are shown in Fig. 4. From the graph it can be observed that the plots can be divided into two regions. On increasing the doping concentration, the conductivity is found to vary in a non-linear manner. In the polymer electrolyte [PEO + NaHCO₃], [PEO + NaHCO₃ + Plasticizer] systems, d.c. conductivity is found to be in the order of \sim 10⁻⁷, and 10⁻⁶, respectively. The conductivity values at room temperature(R_T), 373K and the activation energies are given in Table 2, for pure and complexed PEO with NaHCO₃ and PEO with NaHCO₃ + plasticizer (DMF) in different weight ratios.

The ionic transference number has been measured from the polarization current versus time plot, using the equation: $t_{ion} = (i_i - i_f) / i$

Where i_i is the initial current and i_f is the final residual current. Fig. 5. Shows the polarization current versus time plot of PEO + NaHCO₃ and PEO + NaHCO₃ + Plasticizer (DMF) electrolyte systems respectively. The transference number values for all the samples are found to be close to unity indicating that the charge transport is predominantly due to sodium ions whereas the electronic contribution to the charge transport is very small. Mobility of the ionic

species (Na⁺) are measured using transient ionic current method [13, 14]. The mobility is determined using the equation

$$U = d^2 / TV$$

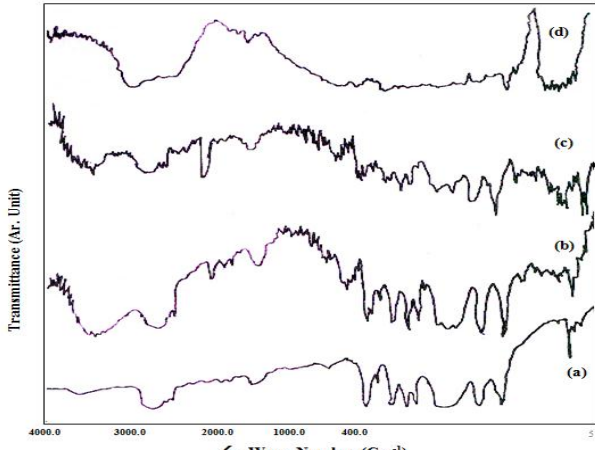


Fig. 1. IR spectra of (a) Pure PEO (b) PEO + NaHCO₃ + Plasticizer(DMF)(90:10) (c) PEO + NaHCO₃ + Plasticizer(DMF) (80:20) (d) Salt NaHCO₃

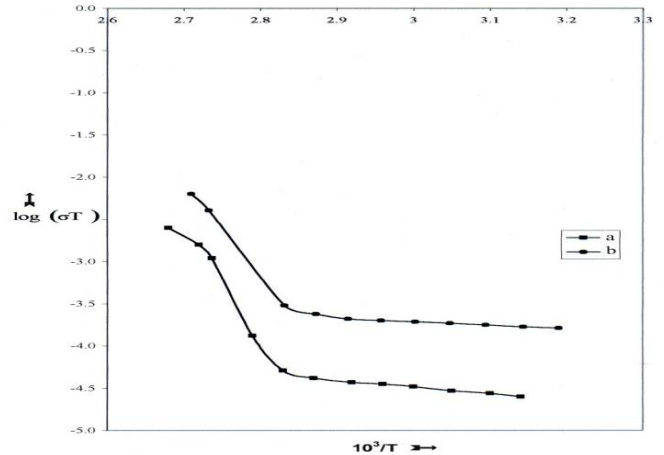


Fig. 4. The temperature dependence of dc conductivity of (a) PEO + NaHCO₃ (80:20) (b) PEO + NaHCO₃+plasticizer (80:20)

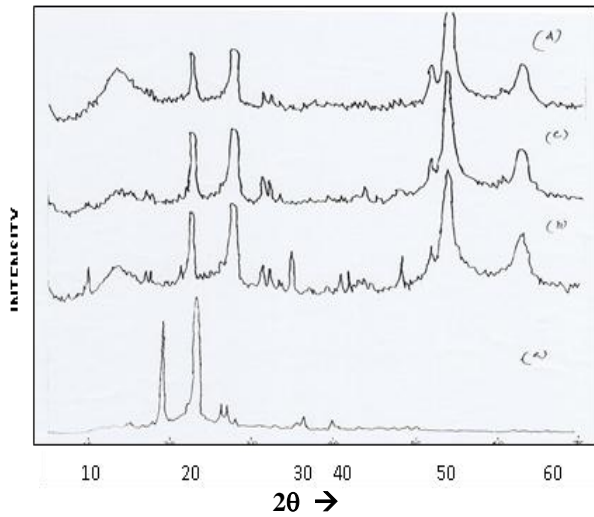


Fig. 2. XRD spectra of (a) Pure PEO (b) PEO + NaHCO₃ (90:10) (c) PEO + NaHCO₃ + plasticizer (80:20) (d) PEO + NaHCO₃ + plasticizer (70:30)

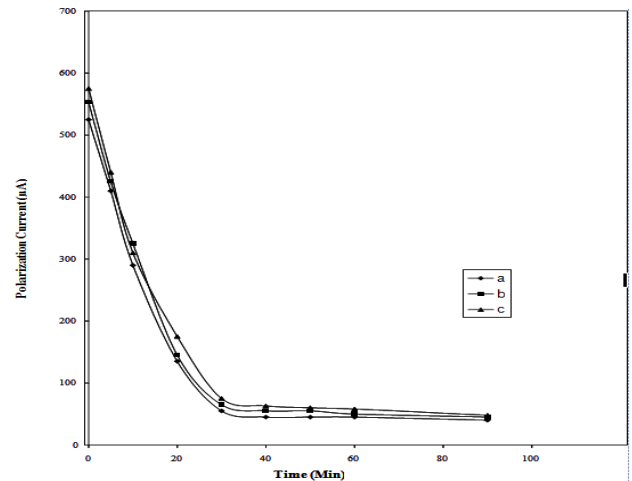


Fig. 5. Polarization current versus time of (a) PEO + NaHCO₃+ plasticizer(DMF) (80:20) (b) PEO + NaHCO₃+plasticizer(DMF) (70:30) (c) PEO + NaHCO₃+plasticizer(DMF) (60:40)

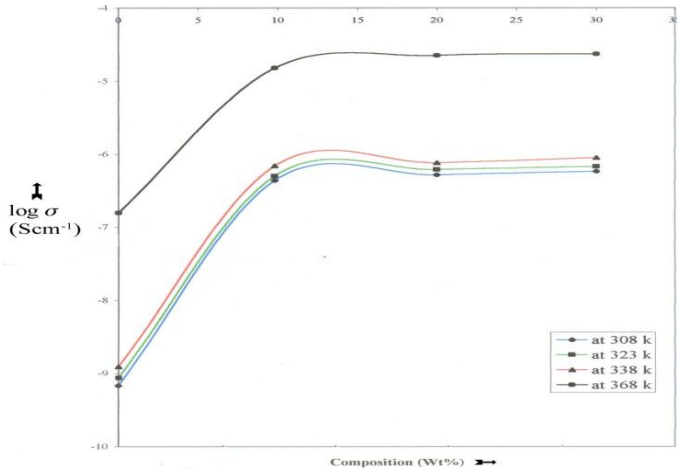


Fig. 3. Composition dependence of conductivity in (PEO + NaHCO₃ + plasticizer) Polymer Electrolyte system at different temperatures.

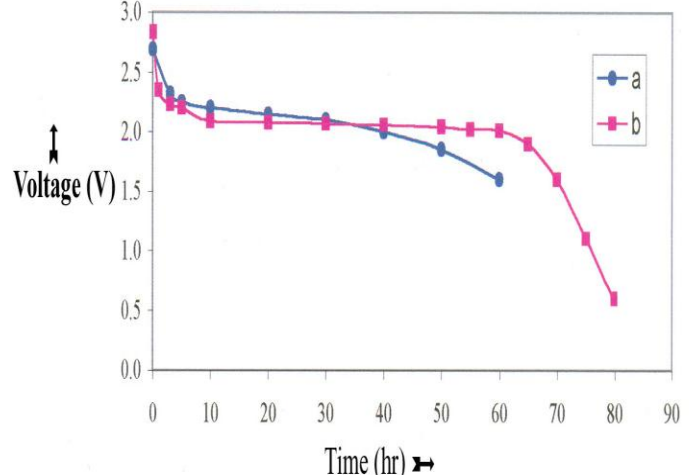


Fig. 6. Discharge Characteristics of an Electrochemical cell for a constant load of 100KΩ

Table 1: Conductivity and Activation Energies for Pure PEO, (PEO + NaHCO₃) and PEO + NaHCO₃ + plasticizer (DMF) electrolyte systems.

Electrolyte	Conductivity at Room temperature (R _T) (S cm ⁻¹)	Conductivity at 373 K (S cm ⁻¹)	Activation Energies in (eV)	
			Region I	Region II
Pure PEO	6.78×10^{-10}	1.58×10^{-7}	0.34	0.38
PEO + NaHCO ₃ (90:10)	1.54×10^{-7}	5.11×10^{-7}	0.32	0.48
PEO + NaHCO ₃ (80:20)	1.62×10^{-7}	5.91×10^{-6}	0.25	0.33
PEO + NaHCO ₃ + DMF (90:10)	0.46×10^{-6}	1.5×10^{-5}	0.29	0.33
PEO + NaHCO ₃ + DMF (80:20)	0.52×10^{-6}	2.2×10^{-5}	0.30	0.31

Table 2. The Values of Mobility and Transference numbers for Pure PEO, (PEO + NaHCO₃) and PEO + NaHCO₃ + Plasticizer (DMF) electrolyte systems

Electrolyte	Transference number (t _{ion})	Mobility (μ) in (cm ² /VS)
Pure PEO	-	0.92×10^{-4} cm ² /VS
PEO + NaHCO ₃ (90:10)	0.92	1.42×10^{-4} cm ² /VS
PEO + NaHCO ₃ (80:20)	0.93	1.61×10^{-4} cm ² /VS
PEO + NaHCO ₃ + DMF(90:10)	0.935	2.11×10^{-4} cm ² /VS
PEO + NaHCO ₃ + DMF(80:20)	0.940	2.16×10^{-4} cm ² /VS

Table 3. Comparison of Present cell / Battery Parameters with data for other Batteries reported earlier.

Electrochemical cell configuration	Open circuit voltage (V)	Discharge time (hours)	Reference
Ag ⁺ /(PEO + AgNO ₃)/ (I ₂ + C + Electrolyte)	0.61	48	[10, 14]
K ⁺ /(PEO + KYF ₄)/ (I ₂ + C + Electrolyte)	2.4	51	[19]
Na ⁺ /(PEO + Glass)/ (I ₂ + C + Electrolyte)	2.1	51	[20]
Na ⁺ /(PEO + NaHCO ₃ + plasticizer)/(I ₂ + C + electrolyte)(80:20)	2.81	79	Present Work

Where d is the thickness of the sample, T is the time of flight, and V is the applied voltage (1.5V). The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) have been evaluated in PEO + NaHCO₃ and PEO + NaHCO₃ + plasticizer systems using Wagner's polarization method [18]. The calculated values of mobility and transference numbers are given in Table 2. The charge transport in these polymer electrolyte films is found to be predominantly due to ions. The variation of ionic conductivity of (PEO + NaHCO₃) and (PEO + NaHCO₃ + Plasticizer (DMF)) electrolyte systems are found to follow the Arrhenius relation.

$$\sigma = \sigma_0 / T \exp(-E_a / KT)$$

Where σ_0 is the pre exponential factor, T is absolute temperature, K is Boltzmann Constant and E_a is the activation energy for the migration of Na⁺ ions.

Solid - state batteries was fabricated with the configuration Na⁺ /polymer electrolyte system (PEO + NaHCO₃ + DMF)/ (I₂ + C + electrolyte). The thickness of the electrode layer is about 1mm. The surface area and the thickness of the electrolyte are respectively 1.34 cm² and 150µm. The discharge characteristics are studied for all the cells at room temperature by connecting a load of 100 KΩ. Fig. 6 shows the discharge characteristic studies of the developed Polymer battery. The initial sharp decrease in the voltage and Current may be due to the polarization effects and / or the formation of a thin layer of sodium salt at the electrode-electrolyte interface [23, 24]. The Open circuit voltage (OCV) and Short circuit current (SCC) for the polymer battery (80:20) are found to be 2.81V and 1.32 mA, respectively. The other cell parameters for this cell were evaluated and summarized below:

Cell weight	= 1.56 gm
Effective area of the cell	= 1.34 cm ²
Thickness of the cell	= 150 µm
Current density	= 0.985 mA/ cm ²
Power density	= 2.46 Watt/ Kg
Energy density	= 194.34 watt-hour/ kg
Discharge time	= 79 hr

The battery parameters calculated for PEO + NaHCO₃ and PEO + NaHCO₃ + plasticizer batteries are given in Table 3 along with the parameters reported for other cells [19-22, 24]. From Table 3 it is clear that the battery parameters are found to be better in plasticizer added

- i) (PEO + NaHCO₃) electrolyte systems, indicating that plasticizer added polymer electrolyte battery exhibit improved battery/cell performance and are more stable than pure polymer electrolyte batteries. Plasticizer added polymer electrolyte systems thus offer an interesting alternative to other reported electrolyte systems for room temperature Solid state Polymer batteries/ electrochemical cells.

4. Conclusions

Plasticizers are of low molecular weight and non-volatile substances (mostly liquids). When a plasticizer is added to a polymer, it improves its flexibility, processability. Thus the utility of plasticizers substantially reduce the brittleness of many polymers, because the addition of even small quantities markedly reduces the melting point (T_m) of the polymer. This effect is due to reduction in the cohesive change. The effect of plasticizer (DMF) on a polymer electrolyte leads to an increase in conductivity by more than a factor of 10 in plasticizer added polymer electrolyte systems when compared with PEO + NaHCO₃ polymer electrolyte systems. Also the plasticizer electrolyte systems show an improved mobility values as compared with the PEO + NaHCO₃ electrolyte systems. From the conductivity data and from Table 2, it is clear that the addition of plasticizer has a remarkable effect on the transport properties of the electrolyte. The solid polymer battery parameters evaluated for plasticizer added PEO + NaHCO₃ complexed electrolyte systems exhibit better results when compared with those for PEO + NaHCO₃ complexed systems, indicating that plasticizer added polymer electrolyte batteries exhibit improved battery performance and higher stability than pure polymer electrolyte systems.

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References

- [1] P.V.Wright. (1975). Electrical Conductivity in Ionic complexes of Poly (ethylene oxide). British Polymer Journal. 7(5) 319-327.
- [2] M.B. Armand, J.M. Chabagno and M.J Duclot. (1979). Fast Ion transport in Solids. Eds.P.Vashista, J.N.Mundy and G.K.Shenoy. North Holland, Amsterdam. Elsevier Applied Science Publishers Ltd. Amsterdam. pp.131.
- [3] S.A.Hasmi, A.Chandra and S.Chandra. (1992). In, Solid State Ionics: Materials and Applications Edited by B.V.R Chowdari. World Scientific. pp.567.
- [4] J.R. Mac Callum and C.A Vincent (Eds.). (1987). Polymer Electrolyte Reviews, Elsevier, Amsterdam.
- [5] J.R.Owen, in; A.L.Lasker and S.Chandra (Eds.). (1989). Super Ionic Solids and Solid Electrolytes-Recent trends, Academic Press, New York. pp.111.

- [6] P.R. Sorenson and J. Jacobson. (1982). Polymer Electrolyte Reviews. *Electrochemical Acta*. 27. pp.1675.
- [7] S. Cristoloveanu and S. S. Li. (1986). Electrical Characterization of silicon on Insulator materials and devices, *Electrochemical Society*. 133: 307.
- [8] Y. L. Lee and B. Crist. (1986). Ionic conductivity of PEO-NH₄ClO₄ films by admittance spectroscopy: Correlation with crystalline and morphology. *Journal of Applied Physics Reviews*. 60: 2683.
- [9] S. Ramalingaiah, D.S. Reddy, M.J. Reddy, E. Lakshminarasaiah and U.V.S. Rao. (1996). Conductivity and discharge characteristic studies of novel polymer electrolyte based on PEO complexed with Mg (NO₃)₂ salt, *Materials Letters*, 29(4-6): 285-289.
- [10] S.S. Rao, K.V.S. Rao, Md. Shareefuddin, U.V. Subba Rao and S. Chandra. (1994). Conductivity and discharge characteristic studies of novel polymer electrolyte based on PEO complexed with Mg(NO₃)₂ salt. *Solid State Ionics*.67:331.
- [11] H.S. Lee, X.Q. Yang, J. Mc Breen, Z.S. Xn, T.A. Skotheim and Y.Okamoto. (1994). A Study of Growth and Surface Performance Analysis of Carbon Nanotubes Grown Using Microwave Plasma Jet Chemical Vapor Deposition System. *Journal of Electrochemical Society*. 141: 886.
- [12] X.Q.Yang, H.S.Lee, L.Hanson, J.Mc Breen and Y Okamoto. (1995). Study of the plasticizer effect on a (PEO+NaYF₄) polymer electrolyte and its use in an electrochemical cell. *Journal of Power Sources*. 54: 198.
- [13] Md. Shareefuddin, Md. Jamal and M. Narasimhachary. (1996). Ionic transport and battery characterization studies of barium-doped potassium yttrium fluoride. *Solid State Ionics*. 83:.229-233.
- [14] S.S. Rao and U.V. S. Rao. (1994). Preparation and characterization of a new polymer battery using PA⁺ AgNO₃ electrolyte. *Material Science Letters*. 13:1771-1772.
- [15] B.L Papke, M.A.Ratnar and D.F.J.Shriver. (1982). Effect of Pressure on conductivity in poly(ethylene oxide) complexed with alkali metal salts. *Journal of Electrochemical Society*. 129:1434.
- [16] K.K Maurya, N.N. Srivastava, N.S. Hashmi and J. Chandra .(1992). Ion transport and battery studies of a new (PVP + KIO₃) polymer electrolyte system. *Journal of Materials Science*. (27): 6357.
- [17] M.J. Reddy, T. Sreekanth, M.C. Sekhar and U.V.S. Rao. (2000). Ion transport and electrochemical cell characteristic studies of a new (PVP + NaNO₃) polymer electrolyte system. *Journal of Materials Science*. 35: 2841-2845.
- [18] J.B. Wagner and C. Wagner. (1957). Electrical Conductivity Measurements on Cuprous Halides. *Journal of Chemical Physics*. 26: 1597.
- [19] E.L. Narasaiah and M. J. Reddy. (1995). Study of a New Polymer electrolyte (PVP+KYF₄) for solid-state electrochemical cells. *Journal of Power Sources*. 55:255-257.
- [20] M.J. Reddy and U.V.S. Rao. (1998). Transport Studies of Poly (ethylene oxide) based polymer electrolyte complexed with sodium yttrium fluoride. *Journal of Materials Letters*. 17:1613-1615.
- [21] M. J. Reddy, T. Sreekanth and U.V. S. Rao. (1999). Ion-conducting polymer electrolyte based on poly (ethylene oxide) complexed with NaNO₃ salt-application as an electrochemical cell. *Journal of Power Sources*. 79(1) 105-110.
- [22] K.V. Kumar and U.V.S. Rao. (2003). Thin Solid electrolyte systems based on PEO and their application as an Electrochemical cell, *Proceedings of 2nd International Conference on Ionic Devices*, 28-30th November 2003, Chennai, India.
- [23] J. S. Kumar, K.V. Kumar, A.R. Subramanyam and M.J. Reddy. (2007). Conductivity study Polyethylene oxide (PEO) complexed with Sodium bicarbonate, *Journal of Material Science*, Springer science, published online: 14 April 2007.
- [24] K.V. Kumar and G. S. Sundari. (2010). Conductivity Studies of (PEO + KHCO₃) Solid Electrolyte system and its application as an Electrochemical Cell – *International Journal of Engineering Science and Technology (JESTEC)*, Malaysia, Taylors University Press, 5(2):130-139.
- [25] K.V. Kumar, G.S. Sundari, M. Chandrasekhar, M. Ashok. (2011). Spectroscopic characterization and Electrical study of Nano Crystalline PEO based conducting polymer electrolyte system for low temperature fuel cell applications- *International Journal of Chemical Technology Research*. 3(3): 1203-1212.