

A COMPARATIVE STUDY OF THE DISCHARGE CHARACTERISTICS OF (PVP/PVA) POLYMER BLEND ELECTROLYTE FILMS DOPED WITH DIFFERENT POTASSIUM SALTS

C.UMADEVI, K.R.MOHAN, A.K.SHARMA

Abstract: Solid polymer electrolyte films based on PVP / PVA polymer blend complexed with KX (X = Cl, Br, I) were prepared by solution cast technique. Electrical conductivity and transport number measurements were used to characterize the polymer electrolyte films. Electrochemical cells with polymer electrolytes (PVP + PVA + KX) were fabricated in the configuration K / (PVP + PVA + KX) / (I₂ + C + electrolyte). The discharge characteristics of the cells were studied under a constant load of 100 kΩ. The open-circuit voltage, short-circuit current and discharge time for the plateau region were measured. Several other cell parameters were evaluated and are compared.

Keywords: Polymer electrolyte film, transport numbers, electrochemical cell, cell parameter.

Introduction: As society becomes increasingly more dependent on electricity, the development of systems capable of storing energy will be a crucial issue for the 21st century. The goal of energy sustainability implies the replacement of all fossil fuels (oil, coal, natural gas) by renewable energy sources (geothermal, biomass, hydrogen, batteries etc.). Many technologies were recently developed for producing, storing and saving electricity; they include metal hydride batteries, lithium and lithium-ion batteries, fuel cells, electrochromic devices, super capacitors etc. All these systems need optimized intercalation compounds. Recently new applications for nano-structured intercalation compounds have been proposed in thin-films, micro-batteries for powering sensors, biomedical devices, credit cards etc.

Electrical conduction can either be due to electronic transport or ionic transport. The solids which possess very high ionic conductivity have been identified since the end of last century [1– 5]. Later, a particular variety of solids exhibiting appreciably high ionic conduction of the order of 10^{-4} to 10^{-1} ohm⁻¹ cm⁻¹ with negligible electronic conductivity at their operating temperature were identified and are named as super ionic conductors or fast ionic conductors or solid electrolytes [6]. The arena of studying such materials is named as solid state ionics and has attracted many scientists from various sectors of physics, electrochemistry, materials science, metallurgy and energy. The study of ionic conduction in various super ionic conductors in the form of single crystals,

amorphous materials, composites, polymeric solids and thin films are widely carried out by the characterization of their physico-chemical properties as well as for technological applications. Because of the widespread use of portable electronic devices, the market for small rechargeable batteries has skyrocketed. Batteries with solid electrolytes are widely in use as they have some extraordinary properties like storage and release of electrical energy, portability, reliability, long life, wide temperature range of operation, mechanical flexibility and high ionic conductivity comparable to liquid electrolytes.

Electrical conductivity: The electrical conductivity in pure (PVP+PVA) and potassium salt doped polymer films was studied as a function of composition of KX and as function of temperature at a fixed field strength.

(a) Composition dependence of dc conductivity: The variation of DC conductivity (σ), as a function of concentration of KX in (PVP+PVA) for different salts is shown in figure 1 at room temperature (300 K).

The variation of dc conductivity σ , as a function of concentration of KCl, KBr and KI in (PVP+PVA) blend is shown in Fig.1 at 300 K. The conductivity dependence for (PVP+PVA+KBr) system is steeper than that observed for (PVP+PVA+KCl) system. The conductivity dependence of (PVP+PVA+KI) system continued to rise with increased dopant concentration in comparison with KCl and KBr doped systems.

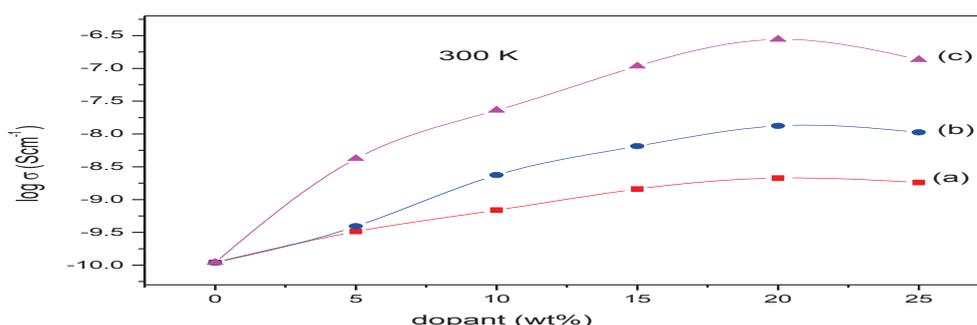


Fig. 1 Composition dependence of dc

conductivity of

(a) (PVP+PVA + KCl) polymer electrolyte system

(b) (PVP+PVA + KBr) polymer electrolyte system

(c) (PVP+PVA + KI) polymer electrolyte system

The conductivity of pure blend was $1.1 \times 10^{-10} \text{ Scm}^{-1}$ at room temperature and its value increased on complexing it with 5% KX. It continued to increase with increased dopant concentration upto 20 wt% of KX although slowly at higher concentrations. After a concentration of 20 wt% of KX the conductivity showed a decreasing trend. The increase in conductivity upto a concentration of 20 wt% of KX may be explained in terms of formation of charge carriers or decrease in the crystallinity of the blend. At higher concentration of KX beyond 20 wt% the decrease in the conductivity may be due to the formation of ionic aggregates at higher dopant concentrations. These ionic aggregates impede the conduction process (7) and decrease the conductivity. The increase in conductivity with increasing dopant concentration upto 20 wt% is attributed to increased ionic mobility and increased ionic charge carrier concentration. The motion of ions in solid polymer electrolytes is a liquid-like mechanism, by which the movement of ions through polymer matrix is assisted by the large amplitude of the polymer segmental motion. The segmental mobility of polymer chains is much higher in amorphous regions than in the crystalline regions [8]. In amorphous regions, the chains are irregular and entangled whereas in crystalline regions the chains are regularly arranged. Hence, it is very easy to move the molecular chains in amorphous state rather than the crystalline state.

The conductivity data of (PVP+PVA+KX) polymer electrolyte systems for various compositions at 300 K is given in Table 1.

From the table it was evident that 20 wt% KX doped (PVP+PVA) blend electrolytes exhibited optimum conductivity. Hence the variation of conductivity as a function of temperature was carried out only on 20 wt% KX doped blends for different salts.

b) Conductivity – Temperature plots:

Fig. 2 shows the variation of electrical conductivity as function of temperature for pure (PVP+PVA) blend and for 20 wt% composition of (PVP+PVA+KX) polymer electrolytes in the temperature range 300 K – 400 K. The following salient features were noticed (i) In the temperature range of study, the conductivity was found to increase with increase of temperature in pure blend as well as in 20 wt% composition of (PVP+PVA+KX) polymer electrolyte. The increase in conductivity with temperature can be linked to the decrease in viscosity and hence, increased chain flexibility [9].

(ii) The room temperature conductivity of (PVP+PVA+KI) polymer electrolyte system was higher than that observed in the case of (PVP+PVA+KBr) and (PVP+PVA+KCl) polymer electrolyte systems.

(iii) The conductivity – temperature plots follow Arrhenius type behaviour throughout the temperature range but with three regions (region-I, region-II and-III) having different activation energies. The middle region (region-II) may be due to a transition from a semicrystalline phase to an amorphous phase [10, 11]. In polymer electrolytes, change of conductivity with temperature is due to the segmental motion, which results in an increase in the free volume of the system [12, 13]. This increase in

free volume would facilitate the motion of ionic charge [14]. Similar behavior was observed in a number of other films [7, 15-17].

As per Arrhenius relation the dependence of conductivity has the form

$$\sigma = \sigma_0 \exp(-E_a / kT)$$

where σ_0 is the proportionality constant, E_a , the activation energy, and k is the Boltzmann constant. The activation energies were calculated from the slope of these plots and the values are shown in Table

2. These values are found to decrease with increase of salt concentration. This may be due to the fact that the addition of small amounts of dopant forms charge transfer complexes in the host lattice. These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice. This results in a decrease of activation energy. The temperature - conductivity plots exhibits three regions (region I, region II and region III) having different activation energies

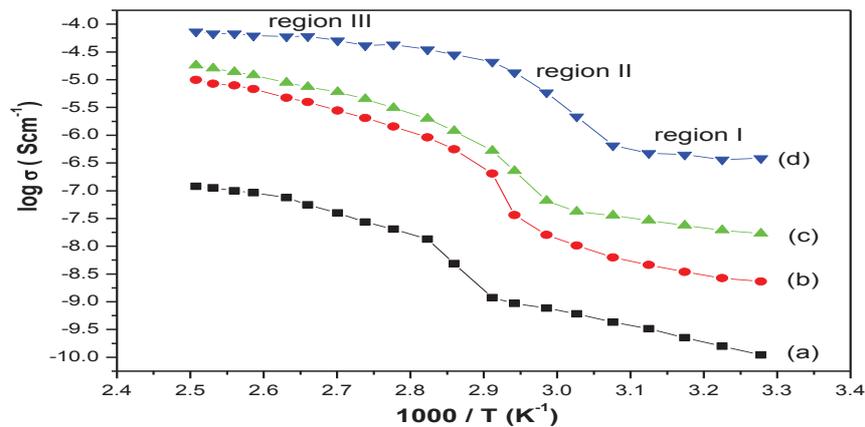


Fig.2 Temperature-dependent

conductivity of

- (a) Pure PVP+PVA (50:50)
- (b) PVP+PVA+KCl (40:40:20)
- (c) PVP+PVA+KBr (40:40:20)
- (d) PVP+PVA+KI (40:40:20)

While regions I and III might be due to intra chain and inter chain segmental motions, region II may be due to the transition of the polymers from the crystalline to amorphous phase [10]. Due to this phase change, the conductivity increases with temperature. Similar behaviour has been reported on polycrystalline p-terphenyl [18], polyacrylic acid [19], polyvinyl alcohol based electrolyte films [10, 20-23]

and PEO based polymer electrolyte films [11- 17, 24 - 28].

Transference numbers: Electronic and ionic transference number measurements play an important role in explaining the conductivity of polymer electrolyte films. Transference numbers of 20 wt% doped (PVP+PVA+KX) electrolyte systems were evaluated using Wagner's polarization technique. In this method, the DC current is monitored as a function of time on application of a fixed DC voltage of 1.5 V across the cell in the configuration K/(polymer blend electrolyte)/C. After polarization, the current versus time plots were drawn (Fig.3).

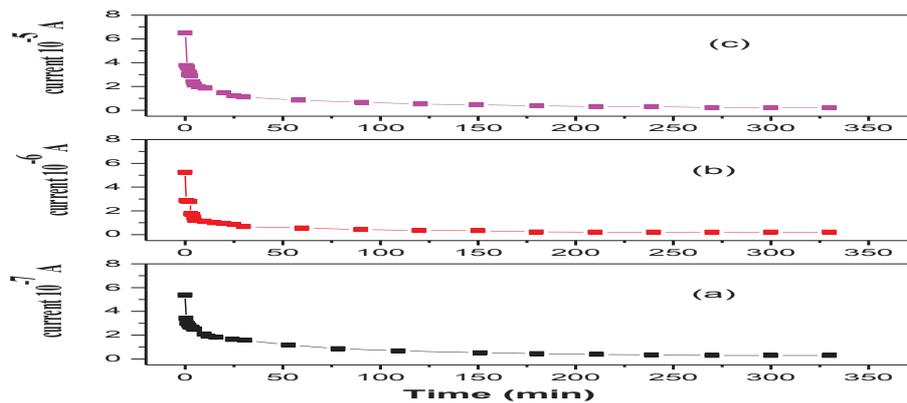


Fig 3 Current vs time plots of

- (a) PVP+PVA+KCl (40:40:20)
- (b) PVP+PVA+KBr (40:40:20)
- (c) PVP+PVA+KI (40:40:20)

The transference numbers were calculated using the relation

$$t_{ele} = I_s / I_t \quad t_{ion} = 1 - I_s / I_t$$

where I_t is the total current (ionic + electronic) at the start of the time (i.e., when $t = 0$) and I_s is the saturation current (electronic current only).

The t_{ion} and t_{ele} values are shown in Table 3. The ionic transference numbers are in the range 0.95 – 0.97. A close look at the transference numbers of these composite films indicates that the charge transport in all these electrolyte systems is predominantly due to ions, only a small fraction of it comes from the electrons.

Discharge characteristics of electrochemical cells: Solid state batteries were fabricated at room temperature using the polymer blend electrolyte films based on (PVP+PVA) complexed with 20 wt% potassium chloride (KCl), potassium bromide (KBr) and potassium iodide (KI). The polymer batteries were assembled in the configuration anode / polymer blend electrolyte / cathode. In the present investigation, potassium metal was used as the anode material in these polymer batteries. The cathode was made in the form of a pellet at a pressure of ~5

ton/cm² after proper mixing of the constituents. Polymer electrolyte was added to enhance the contact properties [29].

The discharge profiles were studied for a constant load of 100 kΩ at room temperature. Fig. 4 shows the discharge characteristics of these polymer batteries. The open circuit voltage (OCV) and short circuit current (SCC) of these cells were measured and are tabulated in Table 4. Various other cell parameters such as current density, plateau region time, power density, energy density etc. were evaluated for different systems and are given in the table.

From Table 4 it is clear that the cell parameters were found to be better in potassium iodide added (PVP+PVA) complexed cell, indicating that potassium iodide added polymer blend electrolyte cells have shown better cell performance and more stability than other polymer blend electrolyte cells.

The data obtained for the present cells compares favourably with the cell parameters of earlier workers on different electrolyte systems [18, 33-42]. This clearly indicates the applicability of the present electrolyte system as a potential candidate for solid state batteries.

- (a) PVP+PVA+KCl (40:40:20)
- (b) PVP+PVA+KBr (40:40:20)
- (c) PVP+PVA+KI (40:40:20)

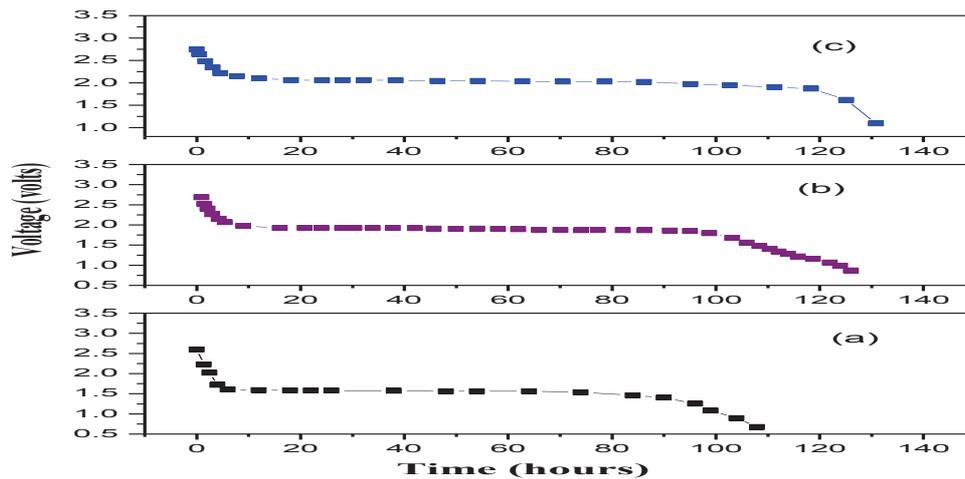


Fig 4 Time vs voltage plots of

Conclusions: The electrical conductivity of pure (PVP+PVA) films at room temperature was of the order of $10^{-10} \text{ Scm}^{-1}$ and varied with salt composition and temperature. The conductivity showed an increase in its value with increasing salt concentration in the polymer. This has been explained in terms of increase in number of mobile ions in the polymer by the addition of the salt. The temperature dependence of conductivity showed an increase in conductivity with increasing temperature in pure as well as complexed polymer electrolytes.

Wagner’s polarization technique was employed to determine the ionic and electronic transference numbers. These numbers showed that the charge transport in these polymer electrolytes is predominantly due to ions with a small contribution from electrons. Electrochemical cells with the configuration anode (K) / polymer electrolyte/ ($I_2 + C + \text{electrolyte}$) (cathode) were fabricated. Among KCl, KBr and KI complexed polymer blend electrolytes, electrochemical cells with KI complexed polymer blend electrolyte showed superior cell parameters.

Table 1 DC conductivity of (PVP +PVA+KX) polymer electrolyte system at room temperature						
Polymer electrolyte system	Conductivity at 300K (Scm^{-1})					
	(50:50:0) (wt %)	(47.5:47.5:5) (wt %)	(45:45:10) (wt %)	(42.5:42.5:15) (wt %)	(40:40:20) (wt %)	(37.5:37.5:25) (wt %)
(PVP+PVA+KCl)	1.10×10^{-10}	3.26×10^{-10}	6.93×10^{-10}	1.45×10^{-9}	2.13×10^{-9}	0.51×10^{-9}
(PVP+PVA+KBr)	1.10×10^{-10}	3.91×10^{-10}	2.37×10^{-9}	6.52×10^{-9}	1.33×10^{-8}	0.93×10^{-8}
(PVP+PVA+KI)	1.10×10^{-10}	4.20×10^{-9}	2.31×10^{-8}	1.08×10^{-7}	2.76×10^{-7}	0.75×10^{-7}

Table 2 Activation energies (E_a) of (PVP+PVA+KX) polyblend electrolyte system			
Polyblend electrolyte system (wt.%)	Activation energy (E_a)		
	Region I (eV)	Region II (eV)	Region III (eV)
(PVP+PVA) (50:50)	0.61	1.90	0.47
(PVP+PVA+KCl) (40:40:20)	0.39	1.27	0.19
(PVP+PVA+KBr) (40:40:20)	0.25	1.06	0.18
(PVP+PVA+KBr) (40:40:20)	0.25	1.06	0.18

Polyblend electrolyte system (wt.%)	Transference number	
	t_{ion}	t_{ele}
(PVP+PVA+KCl) (40:40:20)	0.95	0.05
(PVP+PVA+KBr) (40:40:20)	0.96	0.04
(PVP+PVA+KI) (40:40:20)	0.97	0.03

Cell parameters	(PVP+PVA+KCl) (40:40:20)	(PVP+PVA+KBr) (40:40:20)	(PVP+PVA+KI) (40:40:20)
Open Circuit Voltage (OCV) (V)	2.6	2.69	2.77
Short Circuit Current (SCC) (μ A)	950	1109	1218
Load Resistance ($K\Omega$)	100	100	100
Effective Area of the Cell (cm^2)	1.32	1.32	1.32
Cell Weight (gm)	1.47	1.47	1.48
Discharge Time for Plateau Region (h)	89	98	118
Current Density (μ A/ cm^2)	719	840	923
Power Density (W/kg)	1.68	2.024	2.26
Energy Density (Wh/kg)	141	192	219

References:

1. E. Warburg and Wiedmann, Ann. Physik, 21 (1884) 622
2. E. Warburg, F. Tegetmeier and Wiedmann, Ann. Physik, 32 (1888) 455
3. E. Bruni, O. Scapa and Rend Reale, Accad. Naz. Lincei, 22 (1913) 438
4. C. Tubandt and F. Lorenz, Z. Physik. Chem, 87 (1913) 543
5. C. Tubandt and H. Reinhold, Z. Elektrochem, 29 (1923) 313
6. T. Takahashi (Eds.), in "High Conductivity Solid Ionic Conductors - Recent Trends and Applications", World Scientific, Singapore (1989)
7. Bruce P.G, Synth Met., 45 (1991) 267
8. W.H. Hou, C.Y. Chen and CC. Wang, Solid State Ionics, 166 (2004) 397
9. SS. Sekhon, KV Pradeep and SA Agnihotry, in : B.V.R. Chowdari, K. Lal, S.A. Agnihotry, N. Khare, S.S. Sekhan, P.C. Srivastava, and S. Chandra (eds) "Solid State Ionics : Science and Technology" (World Scientific, Singapore) (1998), p.217
10. R. Chandrasekaran, I.R. Mangani, R. Vasanthi and S. Selladurai, Bulletin of Electrochemistry, 17 (2001) 249
11. R. Huq and G.C. Farrington, Solid State Ionics, 28 (1988) 990
12. M. Armand, J.M. Chabagno and M. Duclot, in : "Fast Ion Transport in Solids", P. Vashista, J.N. Mudy and G. Shenoy (eds.), North Holland, New York (1979) p.131
13. B.C.H. Steele and S.E. Weston, Solid State Ionics, 2 (1981) 347

14. F. Bonino and B.Scrosati, in: "Materials for Solid State Batteries" B.V.R. Chowdari and S. Radha Krishna, (eds) World Scientific Publishing Co., Singapore (1986) p. 42
15. S.A.Hashmi and S. Chandra, Mater. Sci. Eng B, 24 (1995) 18
16. S. Sreepathi Rao, M. Jaipal Reddy, V. Lakshminarasaiah and U.V. Subba Rao, Mater. Sci. Eng. B, 33 (1995) 175
17. K.K.Maurya, S.A. Hashmi and S. Chandra, J.Phy.Soc.Jpn., 61 (1992) 1709
18. R. Bahri and H.P. Singh, Thin Solid Films, 69 (1980) 281
19. V.V.R.Narasimha Rao, T. Mahendar and B. Subba Rao, J.Non-Cryst. Solids, 104(1) (1988) 224
20. P.K.Shukla and S.L. Agrawal, Bulletin of Electrochemistry, 11 (1996) 732
21. S.L. Agrawal and P.K.Shukla, Indian Journal of Pure & Applied Physics, 38 (200) 53
22. P.N. Gupta and K.P.Singg, Solid State Ionics, 86 (1996) 319
23. H.A.Every, F. Zhou, M. Forsyth and D.R.MaxFarlane, ElectrochemiaActa, 43 (1998) 1465
24. K.K.Maurya, N. Srivastava, S.A. Hashmi and S. Chandra, Mater.Soc. Jpn., 27 (1992) 6357
25. S.A. Hashmi, A. Kumar, K.K. Maurya and S. Chandra, J. Phys. D, 23 (1990) 1307
26. S.S. Sekhon and H. Kumar, Bulletin of Electrochemistry, 12 (1996) 750
27. T. Sreekanth, M. Jaipal Reddy, S. Ramalingaiah and U.V. Subba Rao, J. Power Sources, 79 (1999) 105
28. Ch.V.SubbaReddy, A.K.Sharma and V.V.R.Narasimha Rao, J. Power Sources, 111(2002) 357
29. S. Sreepathi Rao, K.V.S.Rao, Md. Shareefuddin, UV.Subba Rao and S.Chandra, Solid State Ionics, 67 (1994) 331

Dr. C.Umadevi/ Department of Physics/S.P.W.Degree& PG College/
Tirupati-517 502/umadevichebiyam@yahoo.in

Dr. K.R.Mohan/ Department of Physics/S.V.University/Tirupati – 517 502
Prof. A.K.Sharma/Department of Physics/S.V.University/Tirupati – 517 502