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Discharge Characteristics of Solid Polmer Blend Electrolyte Films

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Abstract: *Solid polymer blend electrolyte system films on polyvinyl alcohol (PVA) and polyethylene glycol (PEG) complexed with DMF was prepared using solution cast technique. The effect of plasticizer (DMF) on the properties of Sodium ion conducting electrolyte was studied. Complexation of the polymer blend with salt was examined by XRD studies. DC conductivity of the films was measured in the temperature range 303–398 K. The electrical conductivity increased with increasing dopant concentration, which is attributed to the formation of charge transfer complexes. The polymer complexes exhibited Arrhenius type dependence of conductivity with temperature.. The total ionic transport number was evaluated by means of Wagner's polarization technique .Transport number for Sodium ion is ranged from 0.95 to 0.98 depending on the composition. Electrochemical cells with configuration Na / polymer electrolyte / (I_2+C+electrolyte) were fabricated. The discharge characteristics of the cell were studied under a constant load.*

Keywords: *Polymer electrolyte, DC conductivity, Transport number, Electrochemical cell*

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I. Introduction

Solid polymer electrolytes have been extensively studied in the past decades due to their wide potential applications in various electrochemical devices such as solid state batteries, sensors, fuel cells, [1-2]. The electrical conduction in polymer film has much importance due to the discovery of memory phenomenon and has wide applications now-a-days in thin film devices,[3-4].The major efforts in this field have remained concentrated in developing new polymer electrolytes having high ionic conductivity and high mechanical, thermal and electrochemical stability .Various investigations have been performed by blending of polymers, cross linking, insertion of ceramic fillers and plasticization in order to enhance the ionic conductivity [5-6]. Most of the recent research efforts to improve the room temperature conductivity without the fall of mechanical and potential stability have been directed towards the addition of plasticizer such as ethelyne carbonate (EC),prophlene carbonate (PC) and dibutyl pthalate into polymer electrolytes[7-8].The plasticizer interact with the cations and anions and provide additional sites creating favourable high conducting pathways in the vicinity of filler grains for the migration of ions [9]. In the present investigation, polymer electrolytes composing of PVA/PEG as host polymer ,$NaIO_4$ as a salt and dimethyl formamide(DMF) as plasticizer have been prepared .we report here the results of our investigation on the ionic conductivity, transport and discharge studies of polymer blend electrolyte films.

II. Experimental

Films (thickness ~100 µm) of pure blends of (PVA+PEG) and various compositions of complexed films of (PVA + PEG) with $NaIO_4$ salt were prepared in the weight percent ratios (47.5:47.5:5), (45:45:10), (42.5:42.5:15) and (40:40:20) by solution cast technique using tetrahydrfuran as a solvent. DMF was used in small quantity (2 ml) as a plasticizer in these films. The solutions were stirred for 8-10 h to get a homogeneous mixture and were then, cast onto polypropylene dishes and allowed to evaporate slowly at room temperature followed by vacuum drying.

The X-ray diffraction studies were carried out using seifert X-ray diffractometer at room temperature. The dc conductivity was measured by means of an in-house conductivity set-up [10] in the temperature range 303-398 K. The total ionic transport number was evaluated by means of Wagner's polarization technique [11].In this technique, freshly prepared polymer electrolyte films were polarized in the configuration Na/polymer electrolyte/C under a dc bias(step potential of 1.5V). The resulting current was monitored as a function of time. Electrochemical ells were fabricated with a configuration Na/ /(PVA+PEG+$NaIO_4$)/(I_2+C+electrolyte) and Na/ /(PVA+PEG+$NaIO_4$+DMF)/(I_2+C+electrolyte).Details regarding the circuit and electrochemical cell design are given in [12].The open circuit voltage ,short circuit current and discharge time for the plateau region were measured.

III. Results and discussion

3.1. X-ray diffraction

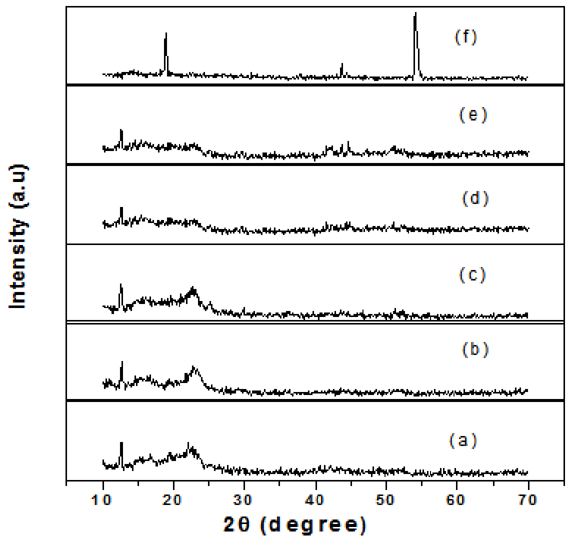


Fig 1. XRD patterns of (a) Pure PVA+PEG (b) PVA+PEG++NalO_4 (47.5 :47.5 :5) (c) PVA+PEG+NalO_4 + DMF (47.5 :47.5 :5) (d) PVA+PEG+NalO_4 (42.5 :42.5 : 15) (e) PVA+PEG+NalO_4 + DMF (42.5 :42.5 :15) (f) NalO_4 salt.

To investigate the complication of Sodium salt with polymer blend XRD studies were performed. Fig. 1 shows the XRD patterns of (PVA+PEG+$NaIO_4$), (PVA+PEG+$NaIO_4$ +DMF) and pure $NaIO_4$ films. Figure 1(a–f) shows peak intensity at $2\theta = 23^0$ for pure blend film. The intensity of this peak decreases with increasing concentration of $NaIO_4$ which implies decrease of degree of crystallization and increase of amorphous nature. Hodge *et al* [13] established a correlation between intensity of the peak and degree of crystalline. The peaks exhibit further decrease in intensity at higher concentrations of $NaIO_4$ salt in the polymer. This indicates a decrease in the crystalline phase with lowering of crystallite size of the polymer electrolyte. The crystalline peaks of 2θ values at 18 and 54^0 corresponding to $NaIO_4$ are absent in nanocomposite polymer bend complexes films. This amorphous nature results in greater ionic diffusivity and high ionic conductivity, which can be observed in amorphous polymers having flexible back-bone [14-15]. This behaviour demonstrates that complication between PVA,PEG, $NaIO_4$ and plasticizer occurs and takes place in the amorphous phase.

3.2 Temperature dependent DC conductivity

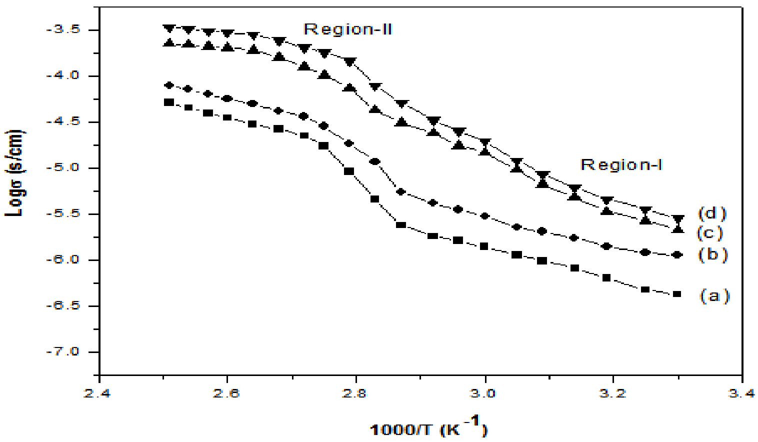


Fig 2. Temperature dependent conductivity of (a) PVA+PEG++$NaIO_4$ (47.5 :47.5 :5)(b) PVA+PEG+$NaIO_4$ +DMF (47.5 :47.5 :5) (c) PVA+PEG+$NaIO_4$ (42.5 :42.5 : 15)(d) PVA+PEG+$NaIO_4$ + DMF (42.5 :42.5 :15)

The variation of dc conductivity as a function of inverse temperature for different composition of (PVA+PEG+$NaIO_4$) , (PVA+PEG+$NaIO_4$+DMF) polymer electrolyte in the temperature range of 303-398 K is shown in the Fig 2. The conductivity is found to increase with increase of temperature in polymer blend as well as in all the compositions of (PEA+PEG+$NaIO_4$) polymer electrolyte. With the addition of plasticizer the conductivity was found to increase when compared to $NaIO_4$ doped films. Plasticizer penetrates the polymer matrix and establish attractive forces with the chain segments, these attractive forces reduce the cohesive force between the polymer chains and increases the segmental mobility which enhance the conductivity. The increase in degree of ionic segmental mobility and interaction between Na ions and the polymer chains induced the higher ionic conductivity in polymer electrolyte system.

The temperature –dependent conductivity plots follow an Arrhenius behaviour throughout with two regions having different activation energies

The conductivity σ may be expressed as

$$\sigma = \sigma_o \exp(-E_a/kT) \qquad .... (1)$$

where σ_0 is the pre-exponential factor, E_a, the activation energy, k, the Boltzmann constant and T is the absolute temperature.

The increase in the conductivity with temperature plots may be attributed to the transition from crystalline/semi-crystalline phase to amorphous phase. The increase in conductivity with temperature is interpreted in terms of a hopping mechanism between coordination sites, local structural relaxation and segmental motion of polymer [16]. As the amorphous region increases, however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favours the hopping inter-chain and intra-chain movements, and the conductivity of the polymer thus becomes high [17].

The activation energies evaluated from the slopes of log σ versus 1000/T plots, for both the regions are given in the Table 1. From the table it is clear that the activation energies in both the regions decrease with the increase of salt concentration in all the samples. Increase in the electrical conductivity and decrease in the activation energy values of polymer electrolytes can be explained on the basis that the polymer films are known to be a mixture of amorphous and crystalline region and the conductivity behaviour of such films may be dominated by the properties of the amorphous regions.

Table 1. DC conductivity and Activation energies of (PVA+PEG+$NaIO_4$) polymer blend electrolyte system at different temperatures

Polymer Electrolyte system (wt %)	**Conductivity(Scm^{-1})**	**Activation Energy(E_a)**	
	303 K	**Region I (eV)**	**Region II (eV)**
PVA+PEG+$NaIO_4$ (47.5 :47.5 :5)	**1.48×10^{-7}**	**0.61**	**0.40**
PVA+PEG+$NaIO_4$ + DMF (47.5 :47.5 :5)	**4.15×10^{-7}**	**0.36**	**0.35**
PVA+PEG+$NaIO_4$ (42.5 :42.5 :15)	**1.68×10^{-6}**	**0.37**	**0.24**
PVA+PEG+$NaIO_4$ + DMF (42.5 :42.5 :15)	**2.11×10^{-6}**	**0.22**	**0.21**

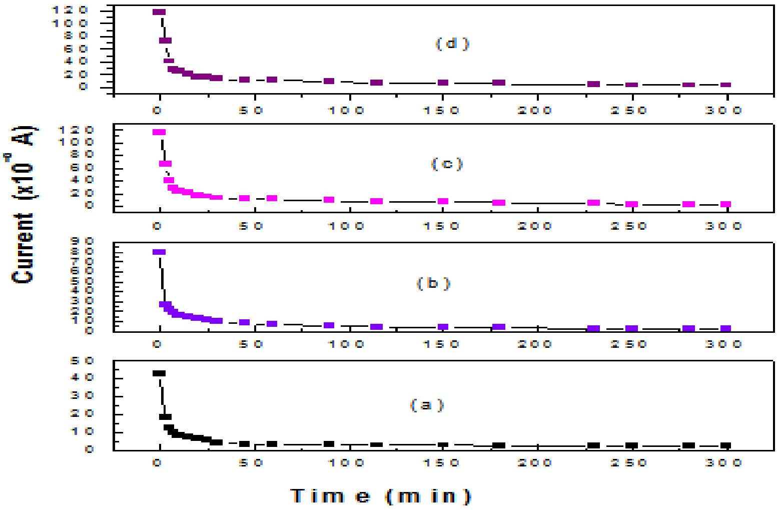
3.4. Transference numbers

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport were evaluated using the Wagner's polarization technique [10]. In this technique, the current is monitored as a function of time on the application of a fixed DC potential of 1.5 V across the cell. The transference numbers were calculated using the following equation

$$t_{ele} = i_s/i_t \qquad .... (2)$$

$$t_{ion} = 1 - \frac{i_s}{i_T} \qquad .... (3)$$

where I_i is the initial current and I_f is the final residual current.



ig.3 Current vs time plots of (a) PVA+PEG+NaIO$_4$ (47.5:47.5:5)
(b) PVA+PEG+NaIO$_4$ + DMF (47.5:47.5:5) (c) PVA+PEG+NaIO$_4$ (42.5:42.5:15)
(d) PVA+PEG+NaIO$_4$ + DMF (42.5:42.5:15)

Figure 3 shows the variation of current as a function of time upon the application of a DC voltage of 1.5 V across the (Na/electrolyte/C) cell. The transference numbers evaluated from the plots are given in Table 2. The ionic transference number was found to be in the range 0.95–0.98 in these polymer electrolyte systems. This suggests that the charge transport in these polymer electrolytes is predominantly due to ions, with negligible contribution from the electrons.

Table 2: Transference numbers of NaIO$_4$ doped (PVA + PEG) polymer blend films.

Polyblend electrolyte	**Transference numbers**	
	t_{ion}	**t_{ele}**
PVA+PEG+NaIO$_4$ (47.5 :47.5 :5)	**0.95**	**0.06**
PVA+PEG+NaIO$_4$+ DMF (47.5 :47.5 :5)	**0.95**	**0.05**
PVA+PEG+NaIO$_4$ (42.5 :42.5 : 15)	**0.97**	**0.03**
PVA+PEG+NaIO$_4$+ DMF (42.5 :42.5 :15)	**0.98**	**0.02**

IV. Electrochemical cell discharge characteristics

Solid state electrochemical cells were fabricated with the configuration (Anode)/polymer electrolyte/(cathode).Discharge characteristics of the cell for a constant load of 100 KΩ were evaluated at room temperature and are shown in Fig.4.The initial sharp decrease in the voltage in these cells may be due to polarization and the formation of thin layer of sodium salt at the electrode-electrolyte interface. The open circuit voltage (OCV),short circuit current(SCC) and other all parameters of these cells are listed in Table 3.The data indicate that the cell parameters are better in the cell with with the plasticizer. This suggests that plasticized polythene electrolyte cell exhibit improved performance and better stability than the pure polymer counterparts.Plasticized polymer electrolytes thus offer an interesting alternative to other reported electrolyte system for room temperature solid –state batteries .

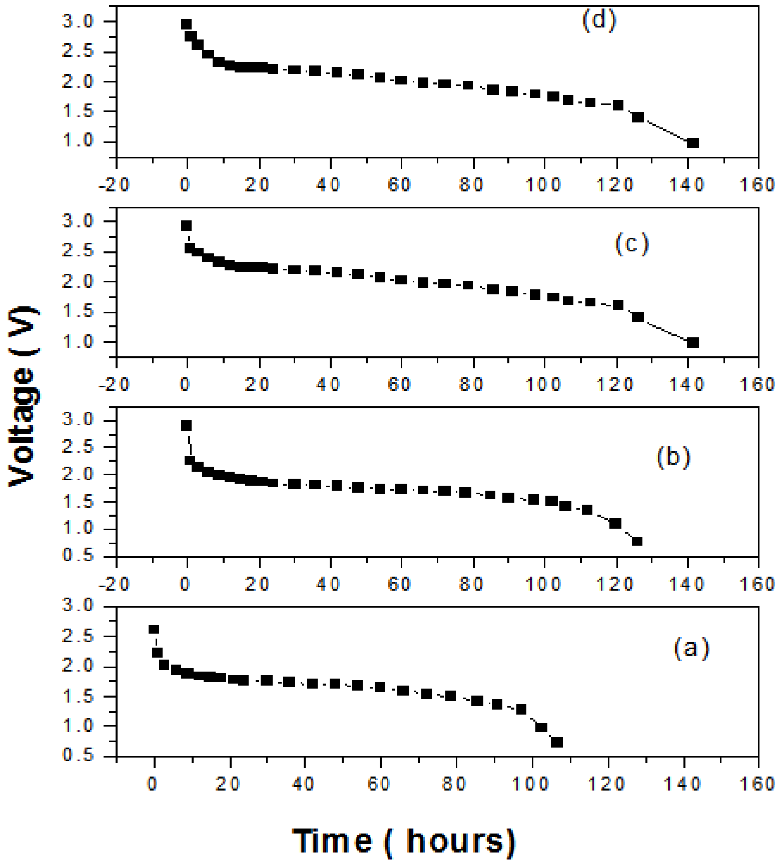


Fig. 4: Discharge characteristics of solid state electrochemical cell with the complexation
(a) Na/PVA+PEG+$NaIO_4$ (47.5 :47.5 :5) / (I_2+C+electrolyte)
(b) Na/PVA+PEG+DMF+$NaIO_4$ (47.5 :47.5 :10)) / (I_2+C+electrolyte)
(c) Na/PVA+PEG+$NaIO_4$ (42.5 :42.5 : 15)/(I_2+C+electrolyte)
(d) Na/PVA+PEG+DMF+$NaIO_4$ (42.5 :42.5 :15)/(I_2+C+electrolyte)
polymer electrolyte system.

Table-3: Various cell parameters of Na/(PVA+PEG+$NaIO_4$ + Plasticizer) / (I_2 + C+ Plasticizer) polymer electrolyte cell system

Cell parameters	**(PVA+PEG+$NaIO_4$) (47.5: 47.5:5)**	**(PVA+PEG+$NaIO_4$ + Plasticizer) (47.5:47.5:5)**	**(PVA+PEG+NaIO4) (42.5 : 42.5 : 15)**	**(PVA+PEG+NaIO4 + Plasticizer) (42.5:42.5:15)**
Open circuit voltage (V)	2.61	2.89	2.92	2.98
Short circuit current (μA)	814	1017	1246	1263
Effective area of cell $(cm)^2$	1.34	1.34	1.34	1.34
Cell weight (grams)	1.40	1.42	1.39	1.41
Time for plateau region (h)	102	120	134	138
Current density $(\mu A/cm^2)$	607	758	929	942
Power density (W/Kg)	1.52	2.07	2.62	2.67
Energy density (Wh/Kg)	154	248	320	368
Load $(K\Omega)$	100	100	100	100

V. Conclusions

The introduction of salts and plasticizer has proved to be a convenient method to increase the ionic conductivity at ambient temperatures. The value of activation energy decreases with increasing dopant concentration and plasticizer. The XRD study reveals the amorphous nature of the polymer electrolytes. The charge transport in these polymer electrolytes is predominantly due to ions, with negligible contribution from the electrons. The plasticized electrolyte films exhibit better performance, which indicates that such electrolytes are more suitable for fabricating sold-state batteries.

References

[1]. B.Scrosats,Electrochim.Acta 45(2000)246
[2]. M.B. Armond, Ann. Rev. Mater. Sci. 16 (1986) 245.
[3]. M.A. Ratner, D.F. Shriver, Chem. Rev. 88 (1988) 109.
[4]. C.A. Vincent, Prog. Solid State Chem. 88 (1989) 109.
[5]. S.Rajendran,M.Sivakumar,R.Subadevi Mater.Lett.58(2004)641.
[6]. S.Ramesh,A.K.Arof,J.Mater.Sci.44(2009) 6404
[7]. Yuan A & Zhao J,Electrochemica Acta,51 (2006)2454
[8]. Wang X L,Mei A,Li M,Lin Y H & Nan C W,J Appl Phys,102(2007) 054907.
[9]. Wieczorek W,Florjanczyk Z & Stevens J R Electrochem Acta,40(1995)2251
[10]. J.B. Wagner, C. Wagner, J. Chem. Phys. 26 (1957) 1597.
[11]. Nadimicherla Reddeppa , A.K. Sharma, V.V.R. Narasimha Rao, Wen Chen. Ionics(2014)
[12]. M.Jaipal Reddy,UV subba Rao,Mater.Lett,23(1995)129
[13]. R.M. Hodge, G.H. Edward, G.P. Simon, Polymer 37(1996) 1371–1376.
[14]. R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T.Hattori, J. Phys. Chem. Solids 68 (2007) 407.
[15]. G.K. Prajapati, P.N.Gupta, Physica B 406 (2011) 3108
[16]. Devendrappa, H., Subba Rao, U.V., and Ambika Prasad, M.V.N. J. Power Sourc., 155 (2)(2006)368.
[17]. Narasimha Rao, V.V.R., Mahendar, T., and Subba Rao, B. J. Non-cryst. Solid., 104 (1)(1988) 224
[18]. N.Reddeppa, A.K. Sharma, V.V.R. Narasimha Rao, Wen Chen Measurement 47 (2014) 33–41
[19]. Anji Reddy Polu & Ranveer Kumar & Hee-Woo Rhee Ionics 20,6(2014)809
[20]. T.uma,T.Mahalingam,J mater sci 39(2004)2901

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