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Polymer Electrolyte Films for Solid State Polymer Batteries

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Abstract:

Solid   polymer electrolyte system films based on polyvinyl alcohol (PVA)   complexed with sodium salt was prepared using solution cast technique. The effect of plasticizer (DMF) on the properties of Sodium ion conducting electrolyte was studied.   DC conductivity of the films was measured in the temperature range 303–398 K. The electrical conductivity significantly increased with addition of plasticizer, 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 0.91 to 0.96 depending on the composition. Electrochemical cells of configuration Na **/** polymer electrolyte **/** (I_2+C+electrolyte) were fabricated. The open circuit voltage,   short circuit current and discharge time for plateau region were measured.

Keywords **— DC conductivity, Transport number, Electrochemical cell, Discharge time.**

1. Introduction

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,[1-2].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 insertion of ceramic fillers and plasticization in order to enhance the ionic conductivity [4].

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[5-6].Plasticizers are low in molecular weight ,non-volatile substances that ,when added to a polymer,improve its flexibility,processibility and ,hence utility.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 [7]. In the present investigation, polymer electrolytes composing of PVA 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 DC conductivity, transport and discharge studies of solid polymer electrolyte films.

2. Experimental

Films (thickness ~120 µm) of pure PVA and various compositions of complexed films of PVA with $NaIO_4$ salt were prepared in the weight percent ratios (95:5), (90:10),

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(85:15) and (80:20) 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 dc conductivity was measured by means of an in-house conductivity set-up [8] in the temperature range 303-398 K. The total ionic transport number was evaluated by means of Wagner's polarization technique [9].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+NaIO$_4$)/(I$_2$+C+electrolyte) and Na/ /(PVA+NaIO$_4$+DMF)/(I$_2$+C+electrolyte).Details regarding the circuit and electrochemical cell design are given in [10].The open circuit voltage ,short circuit current and discharge time for the plateau region were measured.

3. Results and discussion
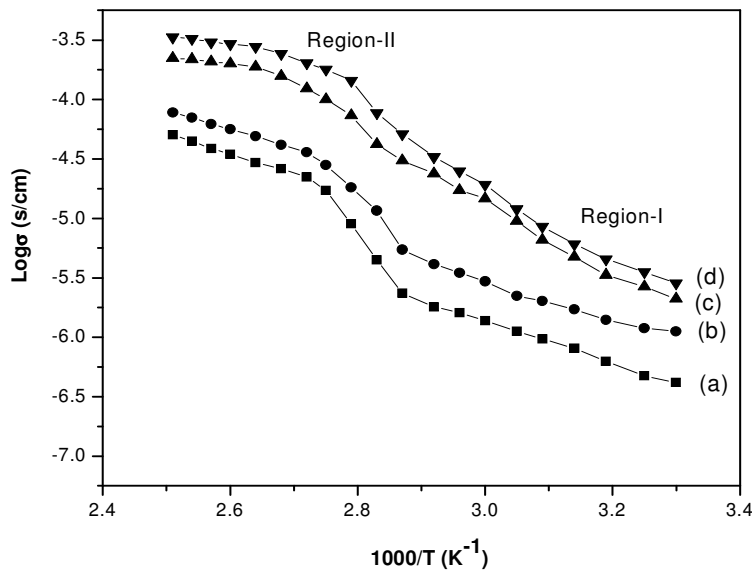### 3.1 Temperature dependent DC conductivity

Fig 1. Temperature dependent conductivity of
(a) PVA+NaIO$_4$ (95 :5)(b) PVA+NaIO$_4$ +DMF (95 :5)
(c) PVA+NaIO$_4$ (85 : 15)(d) PVA+NaIO$_4$ + DMF (85 :15)

The variation of dc conductivity as a function of inverse temperature for different composition of (PVA+NaIO$_4$) , (PVA+NaIO$_4$+DMF) polymer electrolyte in the temperature range of 303-398 K is shown in the Fig 1. The conductivity is found to increase with increase of temperature in all the compositions of (PVA+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

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

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 conductivity with temperature is interpreted in terms of a hopping mechanism between coordination sites, local structural relaxation and segmental motion of polymer [11]. 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 [12].

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+NaIO₄) polymer electrolyte

Polymer Electrolyte system (wt %)	Conductivity(Scm-¹)	Activation Energy(E_a)	
	303 K	Region I (eV)	Region II (eV)
PVA+NaIO₄ (95 :5)	0.54×10^{-7}	0.59	0.40
PVA+NaIO₄ + DMF (95 :5)	4.15×10^{-7}	0.36	0.35

PVA+NaIO$_4$ (85 :15)	1.68×10^{-6}	0.36	0.23
PVA+NaIO$_4$ + DMF (85 :15)	2.19×10^{-6}	0.19	0.21

3.2. Transference numbers

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport were evaluated using the Wagner's polarization technique [8]. 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.
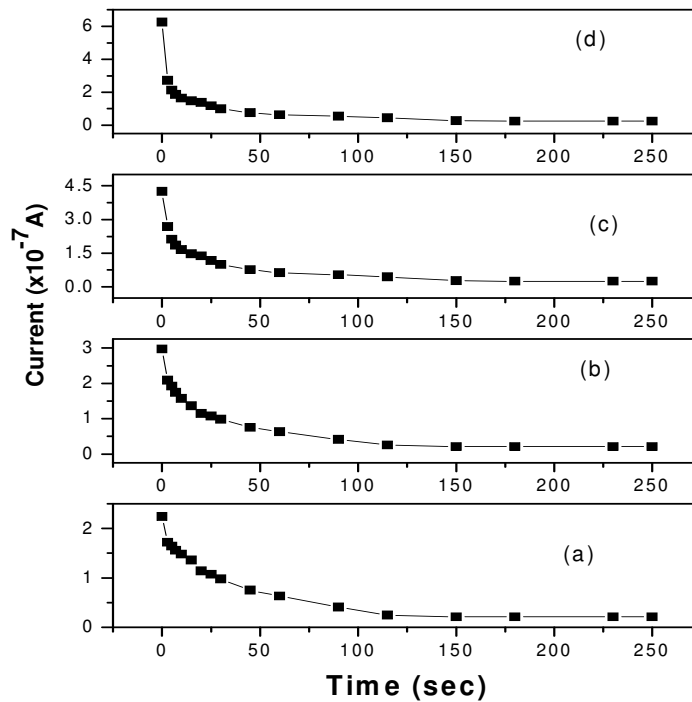

Fig.2 Current vs time plots of (a) PVA+NaIO$_4$ (95:5) (b) PVA+NaIO$_4$ + DMF (95:5) (c) PVA+NaIO$_4$ (85:15) (d) PVA+NaIO$_4$ + DMF (85:15)

Figure 2 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 0.91–0.96 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 NalO$_4$ doped polymer films.

Polymer electrolyte	Transference numbers	
	t_{ion}	t_{ele}
PVA+NalO$_4$ (95 :5)	**0.91**	**0.09**
PVA+NalO$_4$+ DMF (95 :5)	**0.93**	**0.07**
PVA+NalO$_4$ (85 : 15)	**0.94**	**0.06**
PVA+NalO$_4$+ DMF (85 :15)	**0.96**	**0.04**

4. Electrochemical cell discharge characteristics

Solid state electrochemical cells were fabricated with the configuration Na/(PVA+NaIO$_4$)/(I$_2$+C+electrolyte) and Na/(PVA+NaIO$_4$+DMF)/ (I$_2$+C+electrolyte).Discharge characteristics of the cell for a constant load of 100 KΩ were evaluated at room temperature and are shown in Fig.3.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[13-20]. 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 .
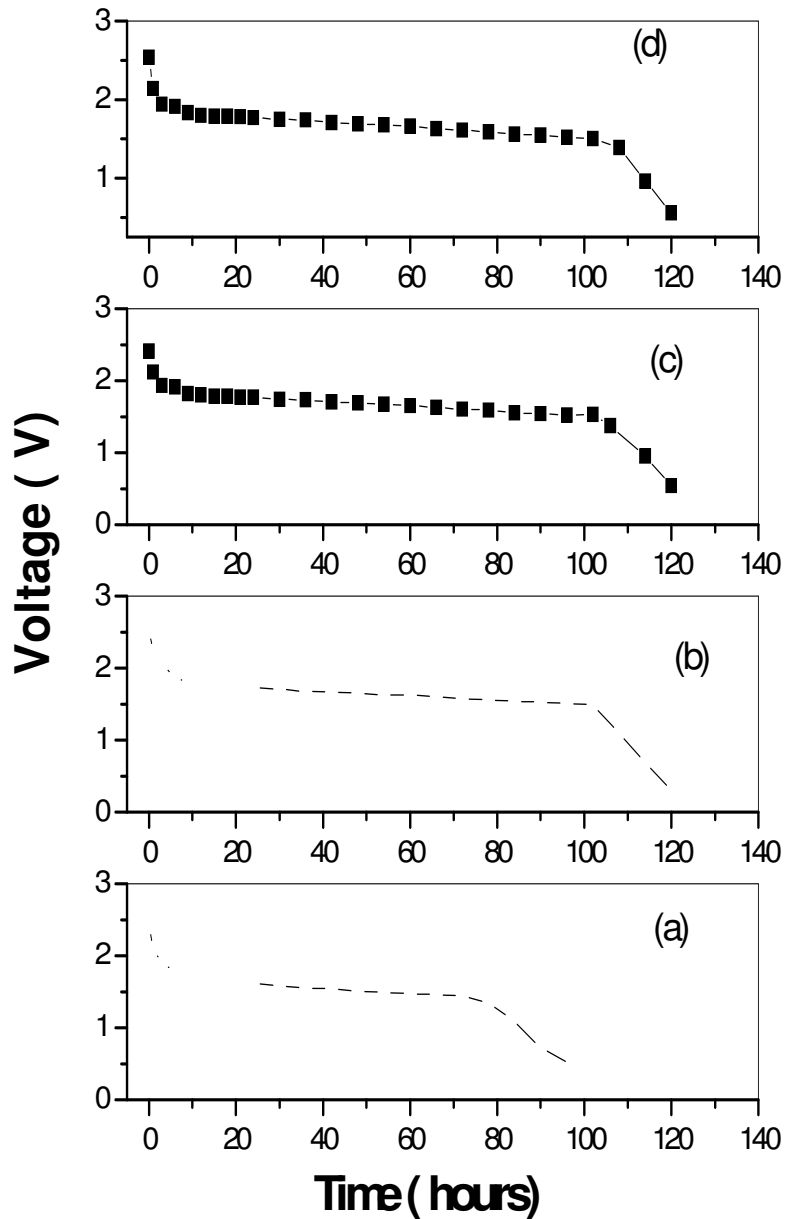
Fig. 3: Discharge characteristics of solid state electrochemical cell with the complexation

(a) Na/PVA+NaIO$_4$ (95 :5) / (I$_2$+C+electrolyte)

(b) Na/PVA+DMF+NaIO$_4$ (95 :5)) / (I$_2$+C+electrolyte)

(c) Na/PVA+NaIO$_4$ (85 : 15)/(I$_2$+C+electrolyte)

(d) Na/PVA+DMF+NaIO$_4$ (85 :15)/(I$_2$+C+electrolyte)

    polymer electrolyte system.

Table-3: Various cell parameters of Na/(PVA+NaIO₄) / (I₂ + C+Electrolyte) polymer electrolyte cell system

Cell parameters	(PVA+NaIO₄) (95:5)	(PVA+NaIO₄ + Plasticizer) (95:5)	(PVA+NaIO4) (85 : 15)	(PVA+NaIO4 + Plasticizer) (85:15)
Open circuit voltage (V)	2.02	2.32	2.41	2.63
Short circuit current (μA)	724	792	812	943
Effective area of cell $(cm)^2$	1.32	1.32	1.32	1.32
Cell weight (grams)	1.41	1.41	1.41	1.41
Time for plateau region (h)	81	98	102	110
Current density $(\mu A/cm^2)$	549	600	615	714
Power density (W/Kg)	1.04	1.31	1.39	1.79
Energy density (Wh/Kg)	84	128	142	197
Load $(K\Omega)$	100	100	100	100

5. Conclusions

The introduction of salts and plasticizer has proved to be a convenient method to increase the DC conductivity at ambient temperatures. The value of activation energy decreases with increasing dopant concentration and plasticizer. 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.

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