

## Characterization of a Solid State Battery Based on Polyblend of (PVP+PVA+KBrO<sub>3</sub>) Electrolyte

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**Abstract.** A potassium ion conducting polyblend electrolyte based on polyvinyl pyrrolidone (PVP) + polyvinyl alcohol (PVA) complexed with KBrO<sub>3</sub> was prepared using solution-cast technique. The electrical conductivity and transference number measurements were performed to characterize the polyblend electrolyte for battery applications. These measurements have shown that the electrolyte is a mixed (ionic + electronic) conductor, the charge transport being mainly ionic ( $t_{ion} = 0.97$ ). Using the electrolyte, electrochemical cells with configurations K / (PVP+PVA+KBrO<sub>3</sub>)/(I<sub>2</sub>), K / (PVP+PVA+KBrO<sub>3</sub>)/(I<sub>2</sub>+C) and K/(PVP+PVA+KBrO<sub>3</sub>) / (I<sub>2</sub>+C+electrolyte) were fabricated and their discharge characteristics studied. The cell with configuration K / (PVP+PVA+KBrO<sub>3</sub>) / (I<sub>2</sub>+C+electrolyte) exhibited better discharge characteristics than the other configurations. The other cell parameters like open circuit voltage (OCV), short circuit current (SCC) etc. were evaluated and are reported.

### 1. Introduction

The field of polymer electrolytes is experiencing vigorous activity in recent years due to significant theoretical interest as well as practical importance for the development of solid state batteries, fuel cells, sensors and electrochemical devices [1-3]. The main advantages of polymeric electrolytes are their mechanical properties, ease of fabrication of thin films of desired sizes and their ability to form proper electrode-electrolyte contact. Most of the earlier studies in this field were devoted to PEO-based electrolytes using alkali salts [4-7], divalent and transition metal cations [8-10] as dopants. Sodium ion conducting polymers have been reported based on PEO, PPO, MEEP complexed with NaI, NaClO<sub>4</sub>, NaSCN, NaCF<sub>3</sub>SO<sub>3</sub> and NaPF<sub>6</sub> [11-15]. Some studies on Ag<sup>+</sup> ion conducting polymer electrolytes based on PEO are reported [16-18]. Several other polymer electrolytes such as PEO + KAg<sub>4</sub>I<sub>2</sub> [19], PEO + Li(ClO<sub>4</sub>) [20] and PEO+NaIF<sub>4</sub> [21] are also reported. Potassium ion conducting polymers have been reported based on PEO complexed with KBrO<sub>3</sub> [22]. All these studies are mainly based on the use of conducting polymers such as PEO, PPO, etc. Some studies on Ag<sup>+</sup> ion polymer electrolyte based on poly-

acrylamide (PA) [23] and polyvinyl pyrrolidone (PVP) complexed with AgNO<sub>3</sub> have also been reported [24]. No reports appear in literature on the development of polyblend electrolytes. Recently, the present authors have reported studies on (PVP+PVA+PEO) electrolyte complexed with KClO<sub>3</sub> [25] and the results have shown considerable improvement in cell properties. In the present paper we report studies on polyblend electrolyte based on polyvinyl pyrrolidone (PVP) + polyvinyl alcohol (PVA) complexed with KBrO<sub>3</sub>. Different experimental studies such as electrical conductivity at room temperature, transport number measurements have been employed to characterize this polyblend electrolyte. Based on this electrolyte, an electrochemical cell has been fabricated and its discharge characteristics studied choosing different cathode materials.

### 2. Experimental Description

Films (thickness ~ 150 μm) of polyblend of (PVP+PVA) and compositions of complexed films of (PVP+PVA) with KBrO<sub>3</sub> were prepared in weight percent ratios (45:45:10), (40 :40:20) and (35:35:30) by solution – cast technique using triple distilled water as a solvent. The solutions was

stirred for 10-12 hours and then cast on to polypropylene dishes and evaporated slowly at room temperature. The final product was vacuum dried thoroughly at  $10^{-3}$  torr.

Solid – state electrochemical cells were fabricated with a configuration of K / (PVP+PVA+KBrO<sub>3</sub>) / (I<sub>2</sub>), K / (PVP+PVA+KBrO<sub>3</sub>)/(I<sub>2</sub>+C) and K/(PVP+PVA+KBrO<sub>3</sub>) / (I<sub>2</sub> + C + electrolyte). Details of the fabrication of the electrochemical cell are same as those employed by Rao et al. [18]. The discharge characteristics of the cells were monitored under a constant load of 100 kΩ.

The dc-conductivity was measured using in-house instrument at room temperature. The ionic and electronic transport numbers ( $t_{ion}$ ,  $t_{ele}$ ) were evaluated by means of Wagner’s polarization technique [26]. In this technique a freshly prepared film of (PVP+PVA+KBrO<sub>3</sub>) was polarized in a configuration of K / (PVP+PVA+KBrO<sub>3</sub>) / C under a dc bias potential of 1.5 V. The resulting current was monitored as a function of time using a Keithley electrometer.

### 3. Results and Discussion

**3.1. Composition Dependence of DC-Conductivity.** The variation dc-conductivity,  $\sigma$ , as a function of composition of KBrO<sub>3</sub> in (PVP+PVA) for different wt % ratios is shown in Fig. 1. The conductivity of uncomplexed (PV+PVA) polyblend was about  $10^{-7}$  Scm<sup>-1</sup> at room at room temperature and it increased on complexing with KBrO<sub>3</sub>. The continuous increase in conductivity with increasing concentration of KBrO<sub>3</sub> is attributed to the decrease in the degree of crystallinity and increase in the degree of amorphosity.

**3.2. Conductivity – Temperature Plots.** Figure 2 shows the variation of electrical conductivity as a function of temperature for pure (PVP + PVA) and for different compositions of (PVP + PVA + KBrO<sub>3</sub>) polyblend in the temperature range 300 - 427 K. The conductivity was found to increase with increasing temperature in both pure and KBrO<sub>3</sub> complexed polyblend electrolyte system. The conductivity – temperature plots followed an Arrhenius behaviour throughout with two regions of activation having different activation energies, above and below the melting point ( $T_m$ ) of the polyblend.

The variation of electrical conductivity ( $\sigma$ ) with temperature (T) can be fitted to the relation [28].

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

where  $\sigma_0$  is a constant, k, the Boltzmann constant and  $E_a$ , the activation energy.

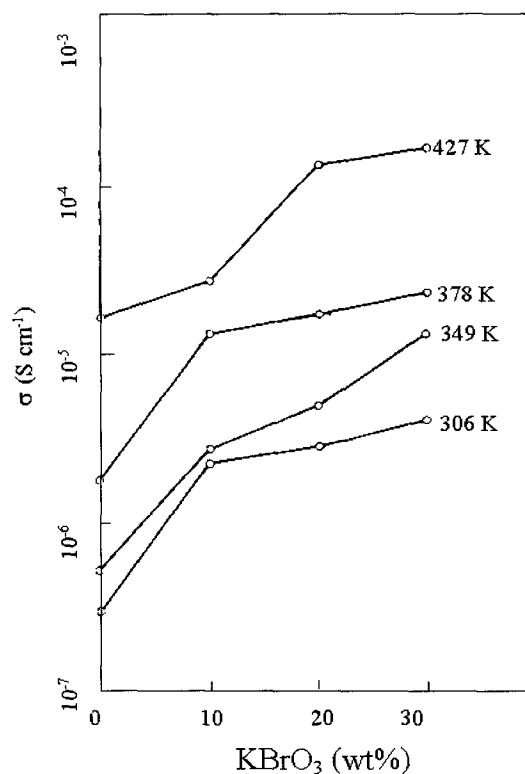


Fig. 1. 1. Composition vs. conductivity plots of (PVP+PVA+KBrO<sub>3</sub>) polyblend electrolyte system at different temperatures.

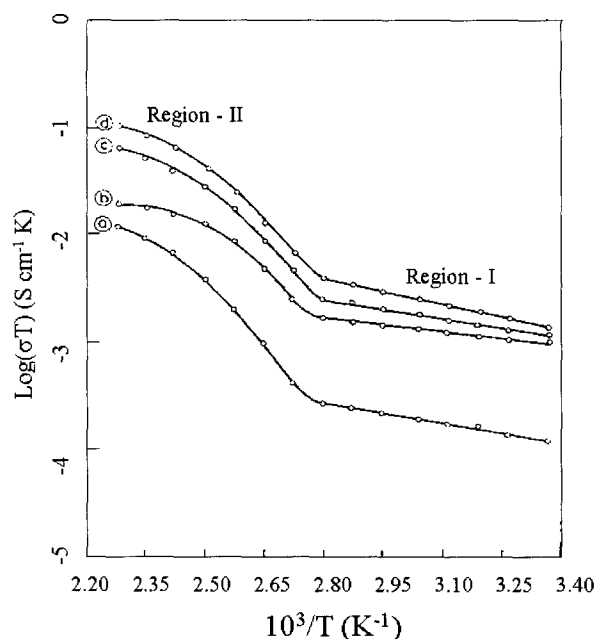


Fig. 2. Temperature dependent conductivity of (a) pure (PVP+PVA) (50:50); (b) (PVP+PVA+KBrO<sub>3</sub>) (45:45:10); (c) (PVP+PVA+KBrO<sub>3</sub>) (40:40:20); (d) (PVP+PVA+KBrO<sub>3</sub>) (35:35:30).

Table 1. Activation energies ( $E_a$ ) for (PVP + PVA) and (PVP + PVA +  $\text{KBrO}_3$ ) polyblend electrolyte system.

Polyblend electrolyte system (wt.%)	Region-I $E_a$ (eV)	Region-II $E_a$ (eV)
(PVP + PVA) (50:50)	0.19	0.49
(PVP + PVA + $\text{KBrO}_3$ ) (45:45:10)	0.12	0.33
(PVP + PVA + $\text{KBrO}_3$ ) (40:40:20)	0.13	0.37
(PVP + PVA + $\text{KBrO}_3$ ) (35:35:30)	0.17	0.43

The activation energies ( $E_a$ ) evaluated from these plots for (PVP + PVA) and (PVP + PVA +  $\text{KBrO}_3$ ) complexes are summarized in Table 1.

The existence of two regions (region I and region II) in the conductivity – temperature plots and the sudden increase in the conductivity at  $T_m$  may be attributed to the transition from semi-crystalline phase to amorphous phase. Due to this phase change, the conductivity shows a sudden increase at  $T_m$  of the polyblend system. Below  $T_m$  (region I) the increase in conductivity with temperature is interpreted as a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polyblend.

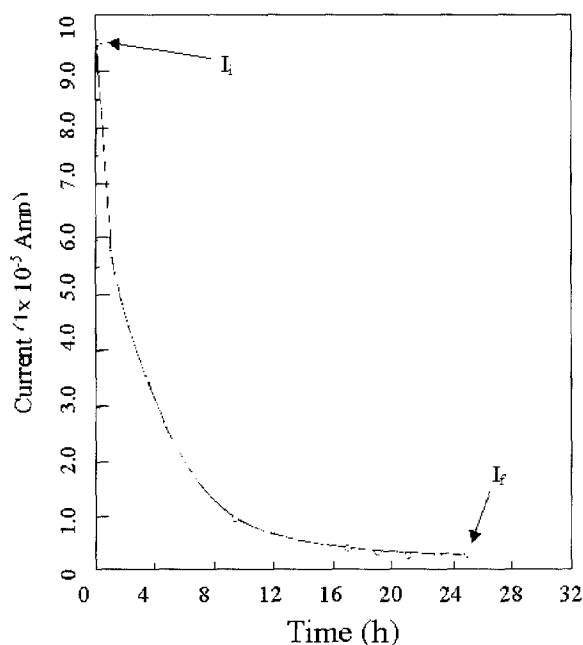


Fig. 3. Current vs. time plots of (PVP+PVA+ $\text{KBrO}_3$ ) (35:35:30) polyblend electrolyte system.

As amorphous regions progressively increase (region II), however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favours the inter chain and intra-chain ion movements and, accordingly, the conductivity – temperature plots has also been observed in (PVP+PVA+PEO) based polyblend electrolyte system [25].

3.3. *Transference Numbers.* The plots of polarization current as a function of time for the electrolyte (PVP+PVA+ $\text{KBrO}_3$ ) of (45:45:20), (40:40:20), (35:35:30) compositions are given in Fig. 3. The transference numbers ( $t_{ion}$  and  $t_{ele}$ ) were calculated from these plots using the equations,

$$t_{ion} = (I_i - I_f) / I_i$$

$$t_{ele} = 1 - t_{ion}$$

where  $I_i$  is the initial current and  $I_f$ , the final residual current. The resulting data are given in Table 2. For all the compositions of (PVP+PVA+ $\text{KBrO}_3$ ) electrolyte system, the value of ionic transference numbers ( $t_{ion}$ ) are in the range (0.92 to 0.97). This suggests that the charge transport in these polyblend electrolyte films is predominantly due to ions; only a negligible contribution comes from the electrons.

For the preparation of electrochemical cells, three different materials were used as cathode, namely, iodine ( $I_2$ ), iodine + graphite ( $I_2+C$ ) (1:1 ratio) and iodine + graphite + electrolyte ( $I_2+C+electrolyte$ ) (5:5:1 ratio). The cathode was made in the form of a pellet at a pressure of  $\sim 2$  ton/cm<sup>2</sup> after proper mixing of the constituents. Using these cathode materials electrochemical cells with the configurations  $K(anode)/(PVP+PVA+KBrO_3)/I_2(cathode)$ ;  $K(anode)/(PVP+PVA+KBrO_3)/(I_2+C)(cathode)$ ; and  $K(anode)/(PVP+PVA+KBrO_3)/(I_2+C+electrolyte)(cathode)$ ;

Table 2. Transference numbers of (PVP+PVA+ $\text{KBrO}_3$ ) polyblend electrolyte.

Polyblend electrolyte (wt.%)	Transference numbers	
	$t_{ion}$	$t_{ele}$
(PVP+PVA+ $\text{KBrO}_3$ ) (45:45:10)	0.92	0.08
(PVP+PVA+ $\text{KBrO}_3$ ) (40:40:20)	0.95	0.05
(PVP+PVA+ $\text{KBrO}_3$ ) (35:35:30)	0.97	0.03

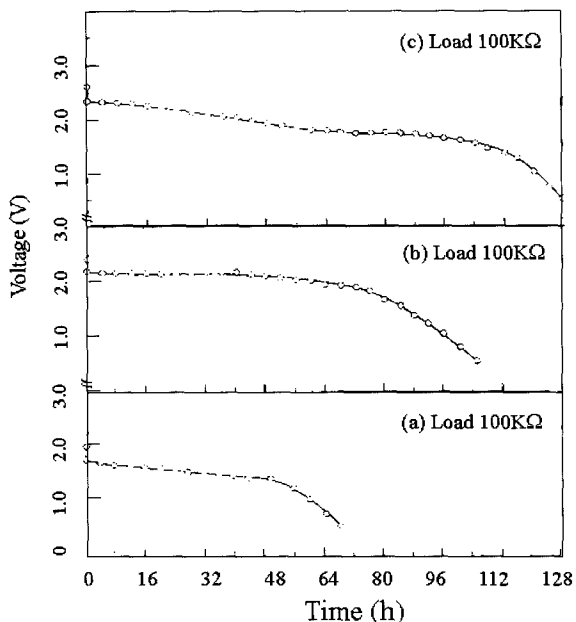


Fig. 4. Discharge characteristics of solid-state electrochemical cell in the configuration of (a) K/(PVP+PVA+KBrO<sub>3</sub>) (35:35:30) / (I<sub>2</sub>); (b) K / (PVP+PVA+KBrO<sub>3</sub>) (35:35:30) / (I<sub>2</sub>+C); (c) K / (PVP+PVA+KBrO<sub>3</sub>) (35:35:30) / (I<sub>2</sub>+C+electrolyte).

were fabricated and their discharge characteristics studied.

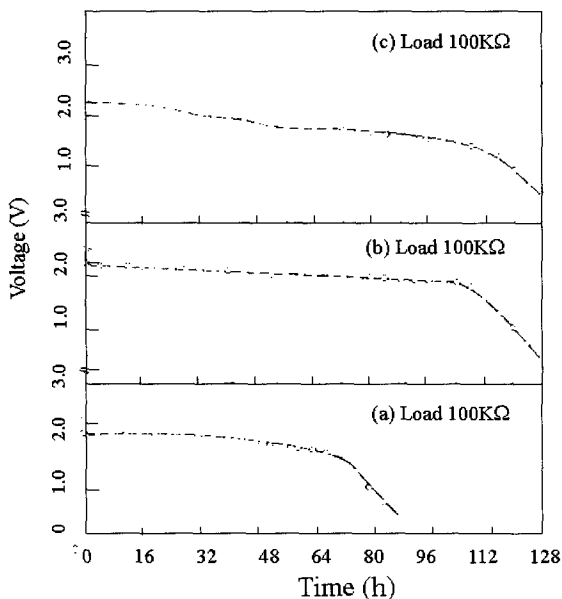


Fig. 5. Discharge characteristics of solid-state electrochemical cell in the configuration of (a) K/(PVP+PVA+KBrO<sub>3</sub>) (45:45:10) / (I<sub>2</sub>); (b) K / (PVP+PVA+KBrO<sub>3</sub>) (40:40:20) / (I<sub>2</sub>+C); (c) K / (PVP+PVA+KBrO<sub>3</sub>) (35:35:30) / (I<sub>2</sub>+C+electrolyte).

Table 3. Various cell parameters for PVP+PVA+KBrO<sub>3</sub> (35:35:30) polyblend electrolyte cells.

Cell parameters	K / (PVP+PVA +KBrO <sub>3</sub> ) / (I <sub>2</sub> )	K / (PVP+PVA +KBrO <sub>3</sub> ) / (I <sub>2</sub> +C)	K / (PVP+PVA+ KBrO <sub>3</sub> ) / (I <sub>2</sub> +C+ Electrolyte)
Open circuit voltage (OCV) (V)	2.25	2.45	2.60
Short circuit current (SCC) (μA)	450	675	920
Load (kΩ)	100	100	100
Discharge time for plateau region (hrs)	54	76	116
Current density (μA/cm <sup>2</sup> )	321	482	657
Effective area of the electrolyte (cm <sup>2</sup> )	1.4	1.4	1.4
Cell weight (gms)	1.72	1.65	1.72
Power density (mW/kg)	16	25	19
Energy density (mW·hr/kg)	879	1911	2185

Figures 4(a), 4(b) and (c) show the discharge characteristics obtained for the above three polymer battery configurations. The cell parameters calculated for these configurations are shown in Table 3. From table it is clear that the cell with the configuration K(anode)/poly blend electrolyte)/(I<sub>2</sub>+C+electrolyte)(cathode) shows better cell performance characteristics and better stability compared to the other two configurations. Hence, in all our studies on potassium based polyblend electrolyte batteries, the above configuration was used.

The discharge profiles of the cells with configuration

- K/(PVP+PVA+KBrO<sub>3</sub>)(40:40:10)/(I<sub>2</sub>+C+electrolyte),
- K/(PVP+PVA+KBrO<sub>3</sub>)(40:40:20)/(I<sub>2</sub>+C+electrolyte)
- K/(PVP+PVA+KBrO<sub>3</sub>)(35:35:30)/(I<sub>2</sub>+C+electrolyte) at

ambient temperature for a constant load of 100 KΩ are shown in Figs. 5 (a), (b) and (c). The initial sharp decrease in voltage of these cells may be due to polarization and/or formation of a thin layer of potassium salt at the elec-

Table 4. Various cell parameters for (PVP+PVA+KBrO<sub>3</sub>) polyblend electrolyte cells.

Cell parameters	(PVP+PVA+KBrO <sub>3</sub> ) (45:45:10)	(PVP+PVA+KBrO <sub>3</sub> ) (40:40:20)	(PVP+PVA+KBrO <sub>3</sub> ) (35:35:30)
Effective area of the electrolyte, cm <sup>2</sup>	1.4	1.4	1.4
Cell weight, (gm)	1.75	1.65	1.72
Open circuit voltage. (OCV), V	2.30	2.54	2.60
Short circuit current (SCC), $\mu$ A	650	850	920
Discharge time for plateau region, h	72	108	116
Power density, mW/kg	19.56	24.8	18.84
Energy density, mWh/kg	1408	2684	2185
Current density, $\mu$ A/cm <sup>2</sup>	464	607	657

trode/electrolyte interface. The anion migration process is limited by the fact that the cathode does not provide a source

of anions to replenish those displaced in the electrolyte. Consequently, depletion of anions from the right hand side of the electrolyte and increase in the concentration on the left hand side means that a concentration gradient opposing the electric field induced migration is set up and the battery becomes concentration polarized with respect to anions. The open – circuit voltage (OCV) and short-circuit current (SCC) and other parameters for these cells are given in Table 4. As the wt.% of KBrO<sub>3</sub> was increased from 10 wt.% to 30 wt.% in the polyblend electrolyte, the performance characteristics of the cell showed an improvement. These parameters are compared with those of other cells reported earlier in Table 5.

A comparison of the present results with other electrolytes based cells clearly indicates that polyblend electrolyte cells based on cheaper polymers (as employed in the present study) compare favorably well with expensive conducting polymers (such as PEO).

#### 4. Conclusions

A new polyblend electrolyte based on (PVP + PVA) complexed with KBrO<sub>3</sub> has been prepared and characterized. The polymer electrolyte is found to be mixed (ionic + electronic) conductor, the charge transport being mainly ionic ( $t_{ion} \sim 0.97$ ). The cells based on this electrolyte with configuration K/(PVP+PVA+KBrO<sub>3</sub>) (I<sub>2</sub>+C+electrolyte) exhibited better discharge characteristics than the other configurations. The cell parameters of these cells compared favorably well with other cells reported in literature.

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Table 5. Comparison of present cell parameters with earlier reported data.

Solid state electrochemical cell configuration	Open circuit voltage. (OCV), V	Short circuit current (SCC) $\mu$ A	Discharge time for plateau region (h)	Reference
K/(PVP+PVA+PEO+KClO <sub>3</sub> )/(I <sub>2</sub> +C+electrolyte)	2.26	1160	65	25
Ag/(PVP+AgNO <sub>3</sub> )/(I <sub>2</sub> +C+electrolyte)	0.46	65	82	24
K/(PVP+PVA+KBrO <sub>3</sub> )/(I <sub>2</sub> +C+electrolyte) (45:45:10)	2.30	650	72	Present
K/(PVP+PVA+KBrO <sub>3</sub> )/(I <sub>2</sub> +C+electrolyte) (40:40:20)	2.54	850	108	Present
K/(PVP+PVA+KBrO <sub>3</sub> )/(I <sub>2</sub> +C+electrolyte) (35:35:30)	2.60	920	116	Present

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