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Short communication

Polymer electrolyte system based on (PEO + $KBrO_3$) — its application as an electrochemical cell

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Abstract

Ion-conducting polymer electrolyte films based on poly (ethylene oxide) (PEO) complexed with potassium bromate ($KBrO_3$) are prepared by a solution-cast technique. Several experimental techniques such as differential scanning calorimetry (DSC), dc-conductivity and transference number measurements are employed to characterise this polymer electrolyte system. The conductivity–temperature plots show two regions in the temperature range of study and transport number data which indicate that the charge transport in this electrolyte system is predominantly due to ions. Using these polymer electrolyte films, solid-state electrochemical cells are fabricated and their discharge characteristics are examined for a constant load of 100 kΩ. Several cell parameters associated with the cells are evaluated and reported. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Conductivity; Transport numbers; Electrochemical cells; Potassium bromate

1. Introduction

Among the various ion-conducting materials, polymer-salt complexes are of current interest on account of their possible application as solid electrolytes in solid electrochemical devices such as energy conversion units (batteries/fuel cells), electrochromic display devices/smart windows, photoelectrochemical solar cells, etc. [1–5]. The main advantages of polymeric electrolytes are their mechanical properties, the ease of fabrication of thin films of desirable size, and their ability to form proper electrode–electrolyte contacts. Poly (ethylene oxide) (PEO), in particular, is an exceptional polymer which dissolves high concentrations of a wide variety of salts to form polymeric electrolytes [6]. The complexes of PEO with a number of alkali salts such as $LiBF_4$, $LiPF_6$ and $LiB(C_6H_5)_4$ [7], LiSCN [8], $LiSO_3CF_3$ and $LiClO_4$ [9], NaSCN [10], $NaPF_6$ [11], $NaYF_4$ and KYF_4 [12] are reported.

Over the past few years, many polymeric electrolytes based on various salts dissolved in polyethers, particularly poly (ethylene oxide) (PEO) have been widely investigated because of their potential viability in high-performance batteries. Such electrolytes have been based mainly on alkali metal salt systems. Special attention has been focused on lithium. Less effort has been made on solid polymer electrolytes and batteries based on potassium complex systems. Apart from scientific interest, the use of potassium has several advantages over lithium counterparts. Potassium is much more abundant and less expensive than lithium. The softness of this metal makes it easier to achieve and maintain contact with other components in the battery. Further, potassium is more moisture-resistant than lithium. Keeping these aspects in view, this study reports a new K^+ ion conducting polymer electrolyte system based on poly ethylene oxide (PEO) complexed with potassium bromate ($KBrO_3$).

2. Experimental

Ion-conducting polymer electrolyte films (thickness: 100–150 μm) of PEO (Aldrich, molecular weight 6×10^5) complexed with $KBrO_3$ salt have been prepared in the weight ratios (90:10), (80:20) and (70:30) by a solution-cast technique using water as solvent. The mixtures of these solutions were stirred for 8 to 10 h, cast on to polypropylene dishes, and evaporated slowly at room temperature. The final products were vacuum dried thoroughly at 10^{-3} mbar to remove all traces of water.

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Differential scanning calorimetry (DSC) curves were recorded in the temperature range 30–120°C using a DSC TA-2010 thermal analysis system at a heating rate of 4°C min^{-1}. The dc-conductivity was measured by means of a laboratory-made conductivity set-up over a temperature range of 303–373 K. The ionic and electronic transport numbers (t_{ion}, t_{ele}) were evaluated using the Wagner polarization technique [13].

Using these polymer electrolyte films, solid-state electrochemical cells were fabricated with the configuration K/(PEO + $KBrO_3$)/(I_2 + C + electrolyte). Details of the fabrication of the electrochemical cells are given elsewhere [14]. The discharge characteristic studies of these cells were monitored for a constant load of 100 kΩ.

3. Results and discussion

The DSC curves of pure PEO and PEO complexed with $KBrO_3$ at a (70:30) composition are shown in Fig. 1. An endothermic peak is observed at 70°C, which corresponds to the melting temperature of pure PEO. The slight shift in the melting point, T_m, towards lower temperatures is due to the addition of $KBrO_3$ salt to the polymer.

The variation of dc conductivity (σ), as a function of the concentration of $KBrO_3$ in PEO is given in Fig. 2 and Table 1. The data reveal, the following features. The conductivity of pure PEO is about 10^{-10} S cm^{-1} at room temperature and its value increases sharply to 10^{-8} S cm^{-1} (i.e. a two-fold increase) at 10 wt.% $KBrO_3$ salt. The increase in conductivity becomes less on further addition of the salt to the polymer.

The variation of conductivity as a function of temperature for different compositions of (PEO + $KBrO_3$) polymer electrolyte system along with pure PEO is given in Fig. 3 for the temperature range 303–373 K. The following features are observed.

1. In the temperature range of study, the conductivity increases with increase in temperature for polymer PEO and for all compositions of the (PEO + $KBrO_3$) polymer electrolyte system.
2. The conductivity–temperature plots follow Arrhenius behaviour throughout, but with two regions (region I and II), above and below melting point (T_m) of the polymer.

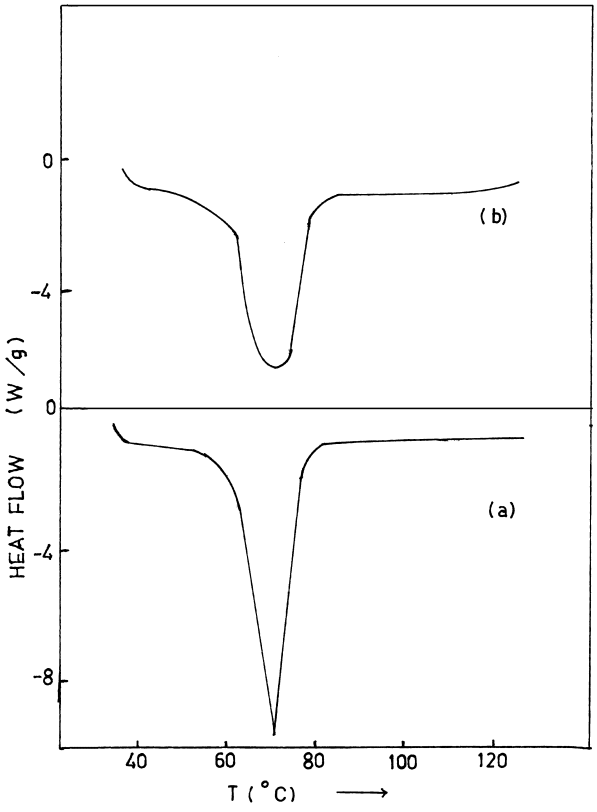

Fig. 1. DSC curves of (a) pure PEO and (b) (PEO + $KBrO_3$) (70:30).

In region I (i.e. below T_m), the conductivity slowly increases with temperature up to 70°C. At this temperature, there is a sudden increase in conductivity. In the region II (i.e. above T_m), the conductivity again increases with temperature. Similar behaviour has been observed in all the compositions of (PEO + $KBrO_3$) polymer electrolyte system.

The temperature T_m, which corresponds to the melting point (70°C) of the polymer, there is a change from a semicrystalline to an amorphous phase. Due to this phase change, the conductivity shows a sudden increase at T_m. The increase of conductivity with temperature is interpreted as being due to a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer. As the amorphous region progressively increases (region II),

Table 1
The dc conductivity and transport number data for (PEO + $KBrO_3$) system

Polymer electrolyte (wt.%)	Conductivity at room temperature (S cm^{-1})	Transport number	
		t_{ion}	t_{ele}
PEO	8.35×10^{-10}	–	–
PEO + $KBrO_3$ (90:10)	1.67×10^{-8}	0.92	0.08
PEO + $KBrO_3$ (80:20)	7.38×10^{-8}	0.95	0.05
PEO + $KBrO_3$ (70:30)	7.74×10^{-8}	0.98	0.02

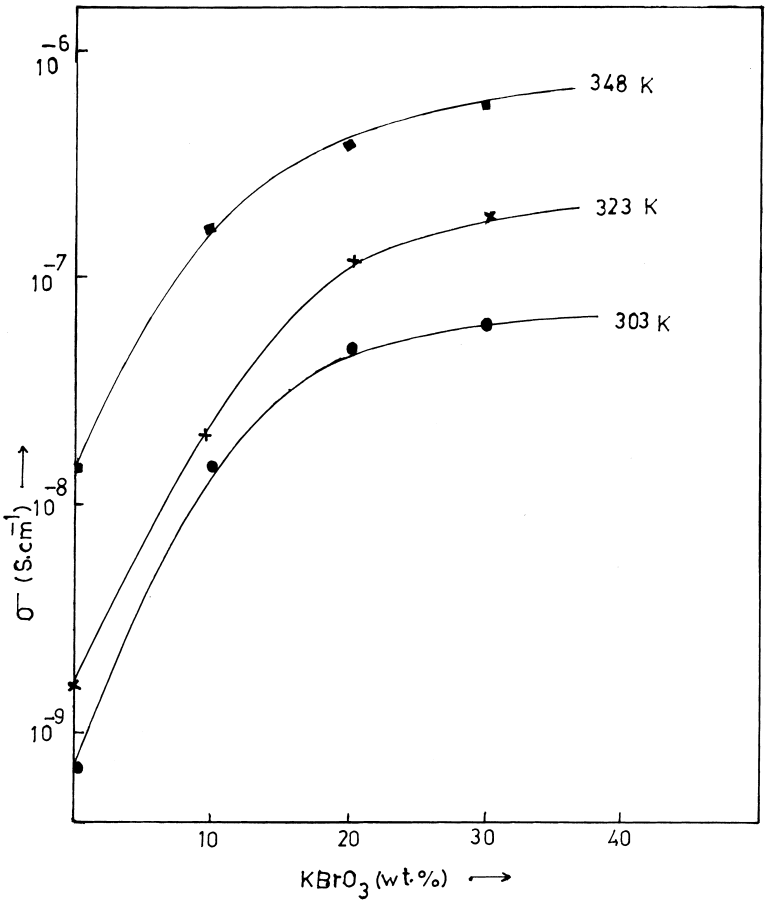

Fig. 2. Composition dependence conductivity of (PEO + $KBrO_3$) system.

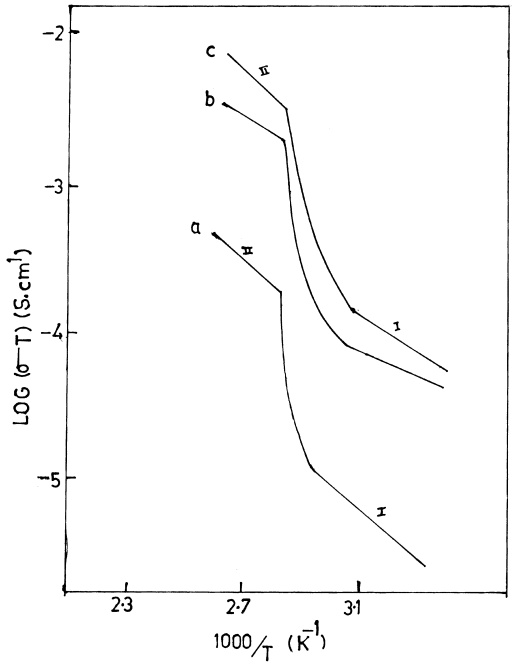

Fig. 3. Temperature dependence of the conductivity of (a) pure PEO, (b) (PEO + $KBrO_3$) (80:20), (c) (PEO + $KBrO_3$) (70:30).

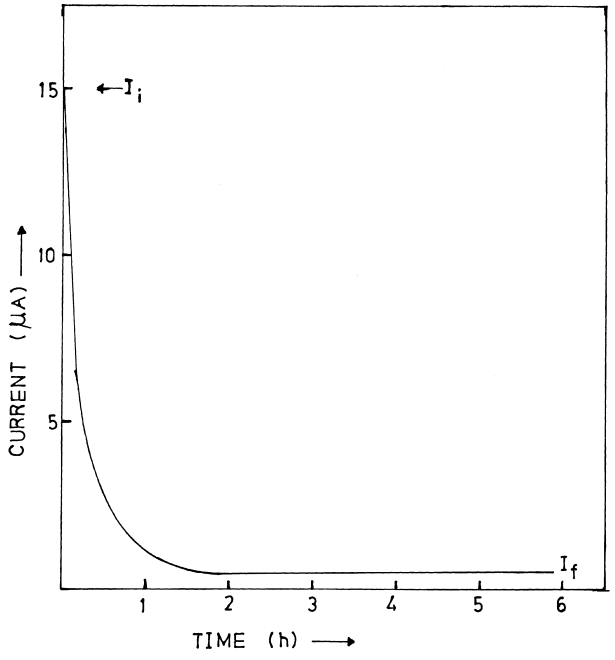

Fig. 4. Current vs. time plot of (PEO + $KBrO_3$) (70:30) composition.

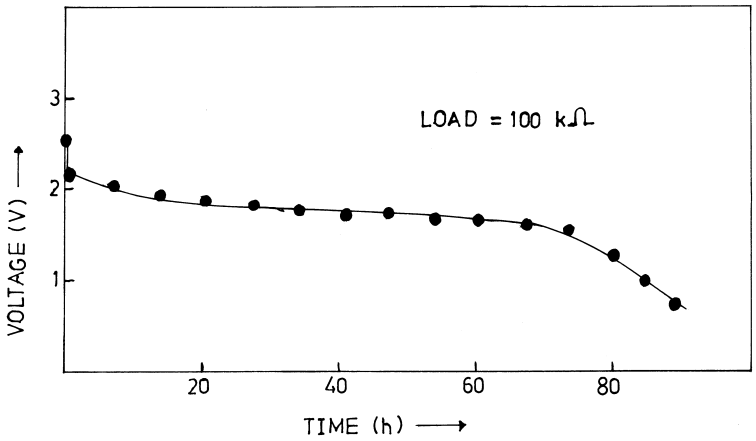

Fig. 5. Discharge characteristics of cell K/(PEO + $KBrO_3$)/(I_2 + C + electrolyte) at room temperature for a constant load of 100 kΩ.

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 ion movements and the conductivity of the polymer electrolyte thus becomes high. The existence of two regions in the conductivity–temperature plots has been observed in a number of PEO-based polymer electrolytes [12,15–17].

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport have been evaluated in (PEO + $KBrO_3$) electrolyte system using Wagner's polarization technique [13]. In this technique, the dc current is monitored as a function of time on application of fixed dc voltage across the K/polymer electrolyte/C cell. After applying 1.5 V, the current versus time plot was obtained, which is shown in Fig. 4 for a (PEO + $KBrO_3$) (70:30) electrolyte. The transference numbers are calculated from the polarization current versus time plot using the equations:

$$t_{ion} = \frac{I_i - I_f}{I_i} \quad (1)$$

$$t_{ele} = \frac{I_f}{I_i} \quad (2)$$

where I_i is the initial current and I_f is the final residual current. The calculated transport number data are given in Table 1. For all compositions of the (PEO + $KBrO_3$) electrolyte system, the ionic transference numbers are found to be in the range 0.92–0.98. This suggests that the charge transport in these polymer electrolyte films is predominantly due to ions.

Using (PEO + $KBrO_3$) polymer electrolyte films, solid-state electrochemical cells were fabricated with the configuration K/(PEO + $KBrO_3$)/(I_2 + C + electrolyte). The discharge characteristics of a cell K/(PEO + $KBrO_3$) (70:30)/(I_2 + C + electrolyte) at ambient temperature for a constant load of 100 kΩ are presented in Fig. 5. The initial sharp decrease in the voltage in these cells may be due to the polarization and/or formation of a thin layer of potassium salt at the electrode–electrolyte interface. The cell parameters evaluated from the discharge curve are:

Open-circuit voltage (OCV)	2.6 V
Short-circuit current (SCC)	125 μA
Load	100 kΩ
Cell weight	1.31 gm
Discharge time for plateau region	72 h
Specific power density	19.69 mW kg^{-1}
Specific energy density	1417.68 mWh kg^{-1}

4. Conclusions

PEO is shown to form a complex with $KBrO_3$ salt which has a high ionic coductivity of the order 10^{-8} S cm^{-1} at room temperature. The conductivity–temperature plots show two regions before and after T_m in the range of temperature studied. Using (PEO + $KBrO_3$) electrolyte, electrochemical cells have been fabricated for which the open-circuit voltage and short-circuit current are 2.6 V and 125 μA, respectively.

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