

Short communication

Conductivity and discharge characteristics of polyblend (PVP + PVA + KIO₃) electrolyte

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Abstract

Films of an ion conducting, polyblend electrolyte based on (polyvinyl pyrrolidone (PVP) + polyvinyl alcohol (PVA)) complexed with KIO₃ are prepared by a solution–cast technique. Measurements of dc conductivity and transference number are made to investigate the order of conductivity and the charge transport in this polyblend electrolyte. Transference number values show that the charge transport in this electrolyte is predominantly due to ions ($t_{\text{ion}} = 0.97$). The magnitude of conductivity increases with increase in the concentration of the salt and temperature. Using this electrolyte, electrochemical cells are fabricated and their discharge characteristics are studied under different loads. The results show that KIO₃ polyblend electrolytes offer interesting alternatives to other solid-state battery systems. The electrochemical decomposition potential (ECDP) is determined for the polyblend electrolyte. From the ECDP studies, the values of open-circuit voltage (OCV) are calculated and are in good agreement with those obtained from discharge studies.

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Keywords: Conductivity; Activation energy; Transference number; Electrochemical cells; Decomposition potential; Polyblend electrolyte

1. Introduction

Polymer electrolytes are an important class of materials and have been used in high energy batteries, fuel cells, gas sensors, display devices, etc. [1–4]. These polymers are preferred to crystalline materials because of their wide range of composition, good interfacial contact between the electrode and electrolyte, and easy preparation in different forms. Polyethylene oxide (PEO), in particular, is an exceptional polymer which can dissolve high concentrations of a wide variety of salts to form polymeric electrolytes [5]. There are reports on the complexes of PEO with a number of alkali salts, e.g. LiBF₄, LiPF₆ and Li(C₆H₅) [6], LiSCN [7], LiSO₃CF₃ and LiClO₄ [8], NaSCN [9], NaPF₆ [10], NaYF₄ and KYF₄ [11]. Investigations have also been made [12–14] on sodium ion conducting polymer electrolyte based on PEO, polypropylene oxide (PPO), and polybismethoxy ethoxy phosphazene (MEEP) complexed with NaI, NaClO₄, NaSCN, NACF₃SO₃. Some Ag⁺ ion conducting polymer complexes with PEO have also been evaluated [15–17]. Reports have appeared on PEO-based electrolytes using divalent cationic salts as dopants [18–21]. The effect of addition of β-Al₂O₃ has been studied in PEO + LiClO₄ [22]

and PEO + NaSCN [23] systems. Chandra et al. [24] have developed a composite polymer electrolyte (PEO + NH₄I + Al₂O₃), which showed improved film stability. Some studies on Ag⁺ ion conducting polymer electrolytes based on PEO [25–27], polyacrylamide (PA) [28] and polyvinyl pyrrolidone (PVP) complex with AgNO₃ have also been reported [29]. Potassium ion conducting polymer based on complexation with KBrO₃ has been examined [30]. By contrast, there have been no published investigations on the development of polyblend electrolytes. Recently, the present authors have reported (PVP + polyvinyl alcohol (PVA) + PEO) electrolyte complexed with KClO₃ [31] and the results have shown considerable improvement in cell properties. In the present work, we report another study on polyblend electrolyte based on polyvinyl pyrrolidone + polyvinyl alcohol complexed with KIO₃. Several experimental techniques such as composition-dependent conductivity, temperature-dependent conductivity in the temperature range 300–427 K and transference number measurements are employed to characterise these polyblend electrolyte films.

2. Experimental

Films (thickness ~150 μm) of a pure blend of (PVP + PVA) and of various compositions of (PVP + PVA) with

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KIO₃ were prepared in the weight percent ratios (45:45:10), (40:40:20) and (35:35:30) with triple distilled water as a solvent using a solution–cast technique. The solutions were stirred for 10–12 h and then poured into polypropylene dishes and allowed to evaporate slowly at room temperature. The final product was vacuum-dried thoroughly at 10⁻³ Torr.

The dc conductivity was measured with an in-house instrument [32] in the temperature range of 300–427 K. The ionic and electronic transport numbers (t_{ion} , t_{ele}) were evaluated by means of the Wagner polarisation technique [33]. In this technique, a freshly prepared film of (PVP + PVA + KIO₃) was polarised in a configuration of KI(PVP + PVA + KIO₃)IC under a dc bias potential of 1.5 V. A Keithley electrometer was used to monitor, as a function of time, the resulting current.

Solid-state electrochemical cells were fabricated with a configuration of KI(PVP + PVA + PEO + KIO₃)|(I₂ + C + electrolyte). Details of the fabrication of the electrochemical cell are given elsewhere [34]. The discharge characteristics of the cells were studied under loads of 100 and 20 k Ω . The cell with configuration KI/polyblend electrolyte|(I₂ + C + electrolyte) was used to determine the electrochemical decomposition potential (ECDP) of the electrolyte. A stabilised variable external voltage was applied. The voltage was changed at a rate of 10 mV s⁻¹ and the corresponding current was measured using a Keithley electrometer.

3. Results and discussion

The variation of dc conductivity, σ , as a function of KIO₃ composition in (PVP + PVA + KIO₃) at various temperatures is given in Fig. 1 and Table 1. The following conclusions can be drawn.

The conductivity of pure (PVP + PVA) is found to be of the order of 10⁻⁷ S cm⁻¹ at room temperature and its variation with composition of KIO₃ is very weak. At higher temperatures, however, the variation is found to be appreciable.

The variation of conductivity as a function of temperature for pure (PVP + PVA) and for different compositions of (PVP + PVA + KIO₃) polymer electrolyte over the temperature range 300–427 K is shown in Fig. 2. The following features are observed:

- (i) The conductivity increases with temperature in pure (PVP + PVA) and also in all the compositions

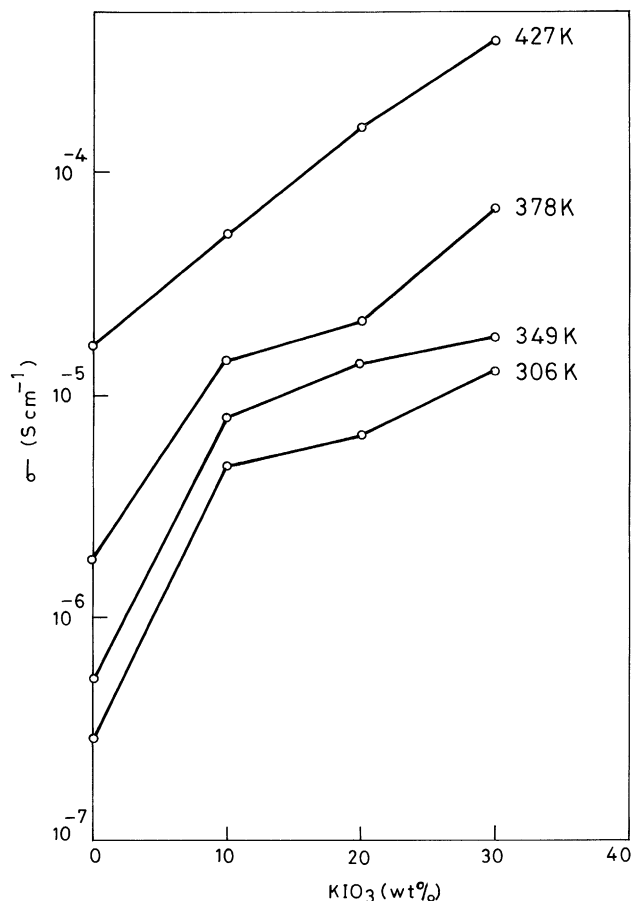


Fig. 1. Composition vs. conductivity plots of (PVP + PVA + KIO₃) polyblend electrolyte system at different temperatures.

of the (PVP + PVA + KIO₃) polyblend electrolyte system.

- (ii) The conductivity versus temperature (σT versus $10^3/T$) plots follow Arrhenius behaviour throughout, but with two regions with different activation energies below (region I) and above (region II) the melting point (T_m) of the polyblend. In region I, the conductivity increases slowly with temperature up to 80 °C, followed by a sudden increase in conductivity. In region II (that is above T_m), the conductivity again increases with temperature. Similar behaviour has been observed for all compositions of the (PVP + PVA + KIO₃) polyblend electrolyte system.

Table 1

Conductivity data of (PVP + PVA) and (PVP + PVA + KIO₃) at different temperatures

Polyblend electrolyte (wt.%)	Conductivity (S cm ⁻¹)			
	306 K	349 K	378 K	427 K
(PVP + PVA) (50:50)	4.61 × 10 ⁻⁷	7.19 × 10 ⁻⁷	2.64 × 10 ⁻⁶	2.21 × 10 ⁻⁵
(PVP + PVA + KIO ₃) (45:45:10)	6.90 × 10 ⁻⁶	9.06 × 10 ⁻⁶	1.87 × 10 ⁻⁵	7.40 × 10 ⁻⁵
(PVP + PVA + KIO ₃) (40:40:20)	9.20 × 10 ⁻⁶	1.52 × 10 ⁻⁵	3.52 × 10 ⁻⁵	1.97 × 10 ⁻⁴
(PVP + PVA + KIO ₃) (35:35:30)	1.22 × 10 ⁻⁵	2.86 × 10 ⁻⁵	8.36 × 10 ⁻⁵	6.99 × 10 ⁻⁴

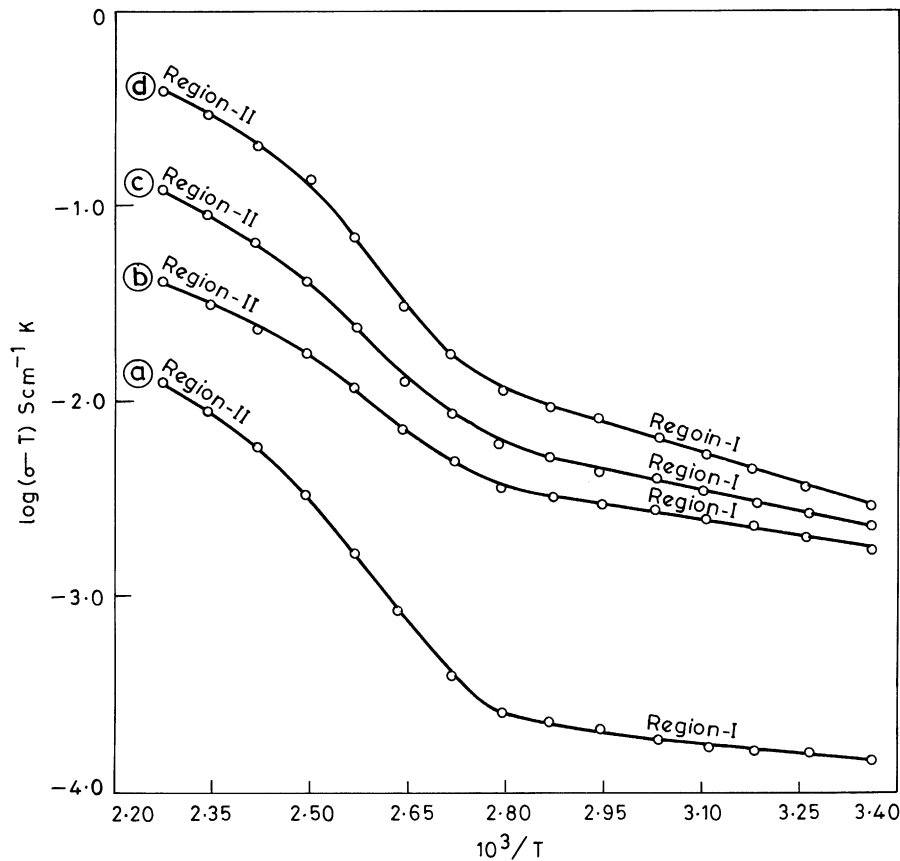


Fig. 2. Temperature-dependent conductivity of: (a) pure (PVP + PVA) (50:50); (b) (PVP + PVA + KIO₃) (45:45:10); (c) (PVP + PVA + KIO₃) (40:40:20); (d) (PVP + PVA + KIO₃) (35:35:30).

Thus, at the melting point ($T_m = 80^\circ\text{C}$) of the polyblend, there is a change from a semi-crystalline to an amorphous phase. Because of this phase change, the conductivity displays a sudden increase. 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 polymer blends. As amorphous regions progressively increase (region II), the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favours hopping inter-chain and intra-chain ion movements and, accordingly, the conductivity of the polymer electrolyte becomes high. The existence of the two regions in the

conductivity–temperature plots has been noticed for a number of PEO-based polymer electrolytes [11,35–38].

The linear variation of σT versus $10^3/T$ plots below and above T_m suggests an Arrhenius-type thermally activated process. The conductivity can be expressed as:

$$\sigma T = (\sigma T)_0 \exp\left(\frac{-E_a}{KT}\right) \quad (1)$$

where $(\sigma T)_0$ is a pre-exponential factor, E_a the activation energy, and K the Boltzmann constant. The calculated activation energies (E_a) and pre-exponential factors $(\sigma T)_0$ for the pure (PVP + PVA) and the (PVP + PVA + KIO₃) polyblend electrolyte systems are given in Table 2.

Table 2
Activation energies (E_a) and pre-exponential factors $(\sigma T)_0$ for (PVP + PVA + KIO₃) polyblend electrolyte system

Polyblend electrolyte (wt.%)	Region I		Region II	
	E_a (eV)	$(\sigma T)_0$ (S cm ⁻¹)	E_a (eV)	$(\sigma T)_0$ (S cm ⁻¹)
(PVP + PVA) (50:50)	0.19	1.90×10^{-1}	0.49	4.52×10^{-3}
(PVP + PVA + KIO ₃) (45:45:10)	0.11	1.37×10^{-1}	0.35	4.33×10^{-2}
(PVP + PVA + KIO ₃) (40:40:20)	0.16	1.14×10^{-1}	0.42	1.58×10^{-3}
(PVP + PVA + KIO ₃) (35:35:30)	0.21	1.00×10^{-1}	0.50	2.53×10^{-5}

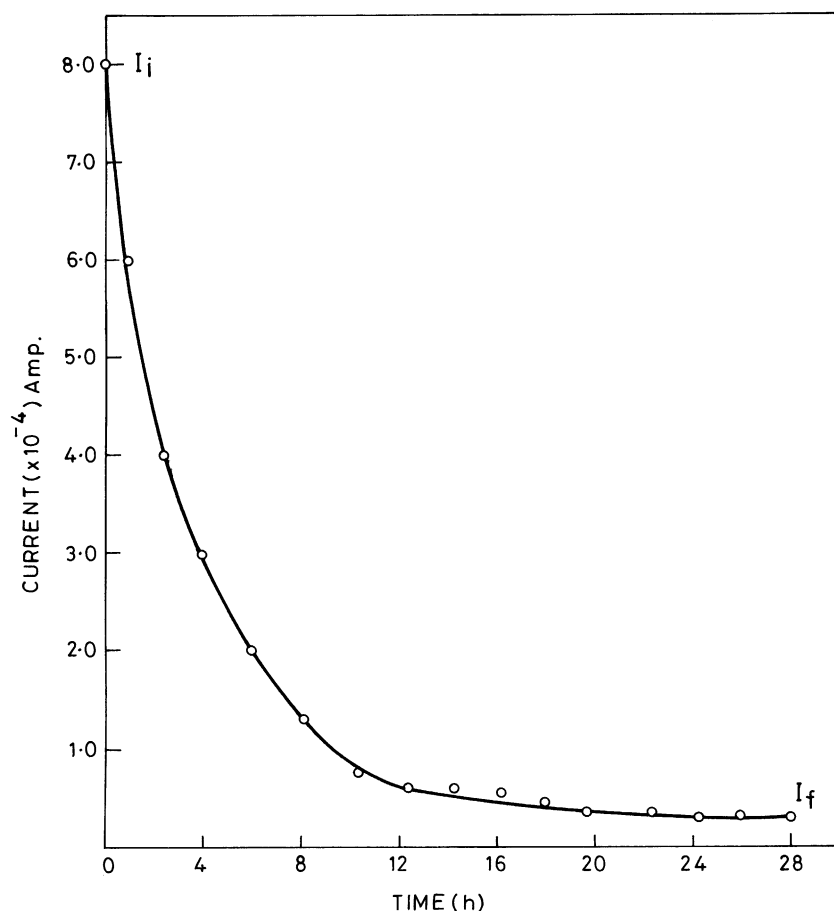


Fig. 3. Current vs. time plot of (PVP + PVA + KIO₃) (35:35:30) system.

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport have been evaluated in the (PVP + PVA + KIO₃) electrolyte system using the Wagner polarisation technique. Plots for (PVP + PVA + KIO₃) with compositions of (45:45:10), (40:40:20) and (35:35:30) are given in Fig. 3. The transference numbers (t_{ion} and t_{ele}) are calculated from the polarisation current versus time plots using the equations:

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

$$t_{ele} = 1 - t_{ion} \quad (3)$$

where I_i is the initial current, and I_f the final residual current. The resulting data are given in Table 3. For all the compositions of the (PVP + PVA + KIO₃) electrolyte system, the ionic transference number (t_{ion}) is in the range 0.92–0.97. This suggests that the charge transport in these polymer blend electrolyte films is predominantly due to ions; only a negligible contribution comes from electrons.

Solid-state electrochemical cells were fabricated with the configuration K (anode)|(PVP + PVA + KIO₃|(I₂ + C +

electrolyte) (cathode) using (PVP + PVA + KIO₃) polyblend electrolyte films. Potassium metal was used as the negative electrode, and a mix of iodine (I₂), graphite (C) and electrolyte in the ratio 5:5:1 as the positive electrode.

The discharge characteristics of KI(PVP + PVA + KIO₃) (45:45:10)|(I₂ + C + electrolyte), KI(PVP + PVA + KIO₃) (40:40:20)|(I₂ + C + electrolyte) and KI(PVP + PVA + KIO₃) (35:35:30)|(I₂ + C + electrolyte) cells at ambient temperature for constant loads of 100 and 20 k Ω are presented in Fig. 4. The initial sharp decrease in voltage of these cells may be due to polarisation and/or formation of a thin layer of potassium salt at the electrode/electrolyte interface.

Table 3
Transference numbers of (PVP + PVA + KIO₃) polyblend electrolyte system

Polyblend electrolyte (wt.%)	Transference number	
	t_{ion}	t_{ele}
(PVP + PVA + KIO ₃) (45:45:10)	0.92	0.08
(PVP + PVA + KIO ₃) (40:40:20)	0.96	0.04
(PVP + PVA + KIO ₃) (35:35:30)	0.97	0.03

The open-circuit voltage (OCV) and short-circuit current (SSC) and other cell parameters for these cells are listed in Table 4. Values of the above parameters for a number of cells reported earlier, together with data for the present polymer electrolyte cells, are given in Table 5. An electrochemical cell was fabricated in the configuration $\text{KI}(\text{PVP} + \text{PVA} + \text{KIO}_3)$ (35:35:30)($\text{I}_2 + \text{C} + \text{electrolyte}$) for determination

of the electrochemical decomposition potential of the electrolyte. A plot of current drawn against applied voltage for this cell is shown in Fig. 5. The intercept of the extended straight line with the x -axis is the electrochemical decomposition potential. The decomposition potential obtained from the plot, viz. 2.5 V, is in good agreement with the observed open-circuit voltage.

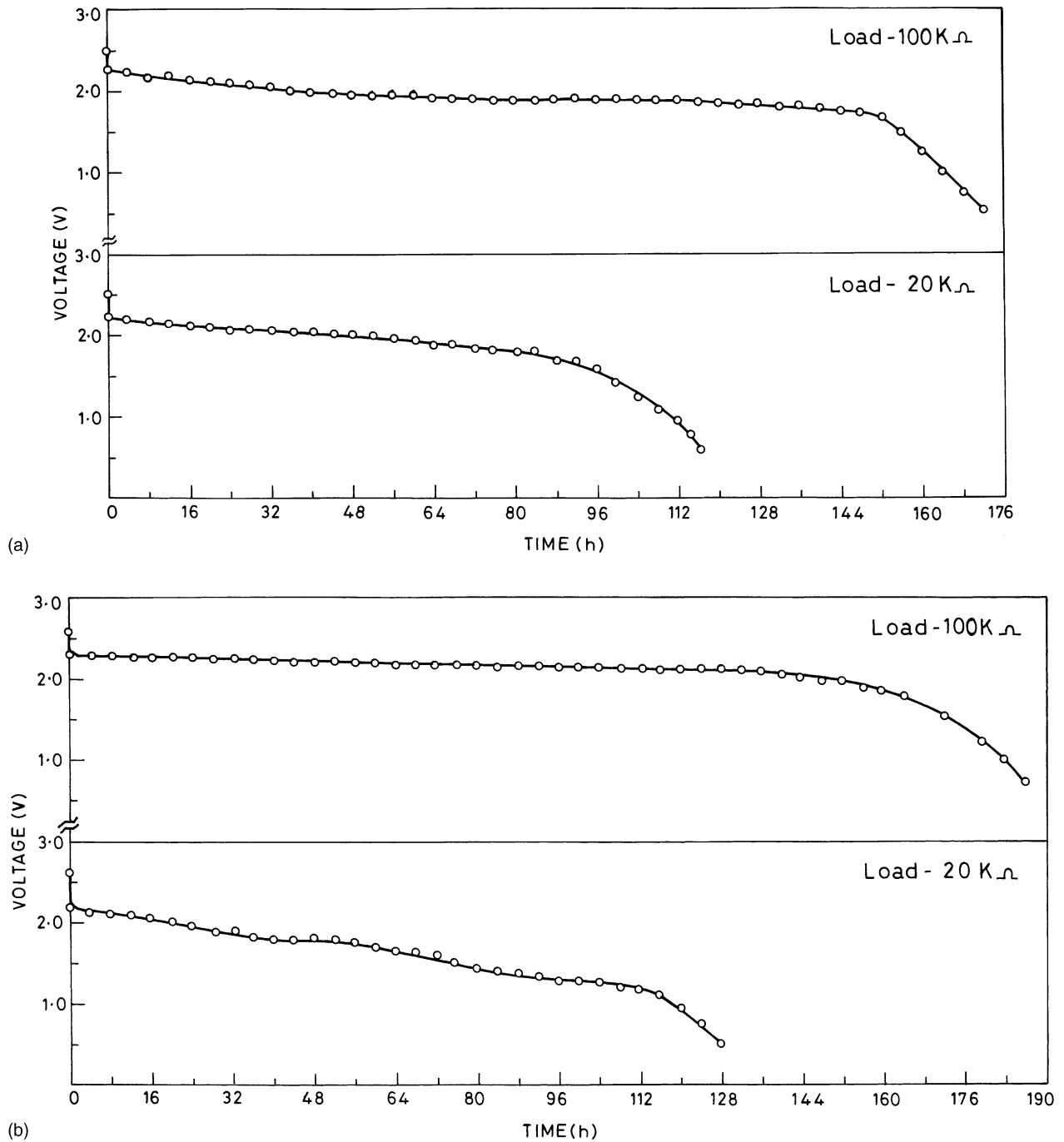


Fig. 4. (a) Discharge characteristics of solid-state cell in configuration of $\text{KI}(\text{PVP} + \text{PVA} + \text{KIO}_3)$ (45:45:10)($\text{I}_2 + \text{C} + \text{electrolyte}$) at loads of 20 and 100 kΩ. (b) Discharge characteristics of solid-state cell in configuration of $\text{KI}(\text{PVP} + \text{PVA} + \text{KIO}_3)$ (40:40:20)($\text{I}_2 + \text{C} + \text{electrolyte}$) at loads of 20 and 100 kΩ. (c) Discharge characteristics of solid-state cell in configuration of $\text{KI}(\text{PVP} + \text{PVA} + \text{KIO}_3)$ (35:35:30)($\text{I}_2 + \text{C} + \text{electrolyte}$) at loads of 20 and 100 kΩ.

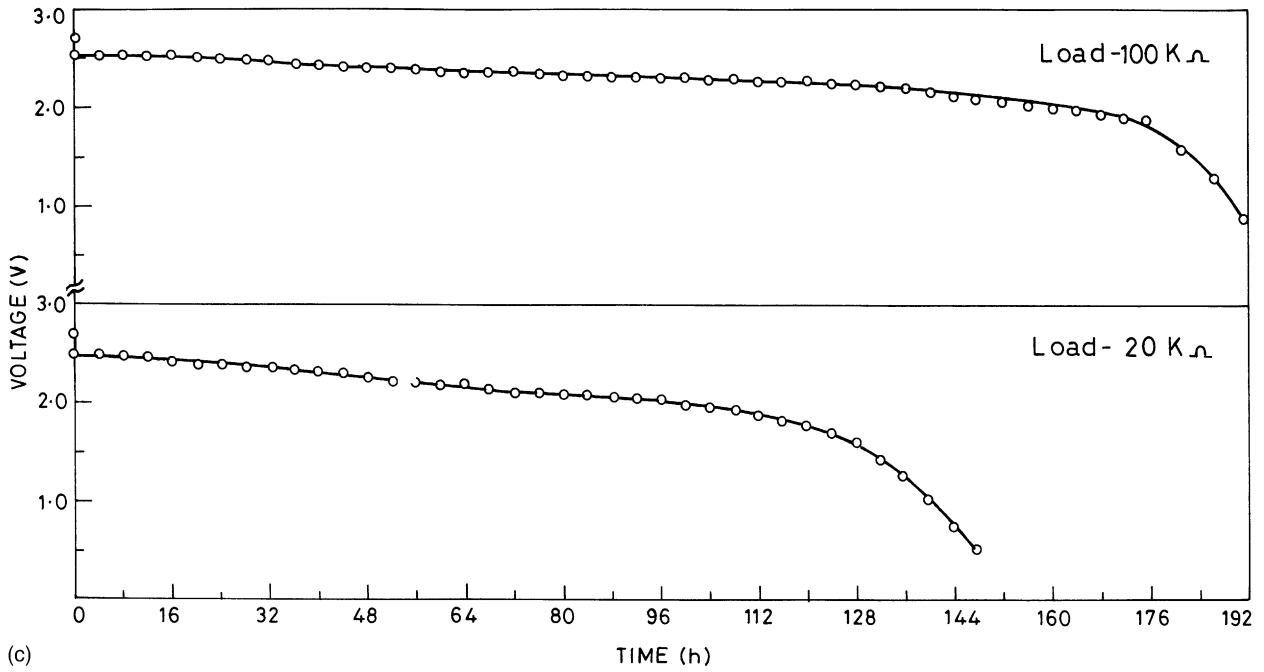


Fig. 4. (Continued).

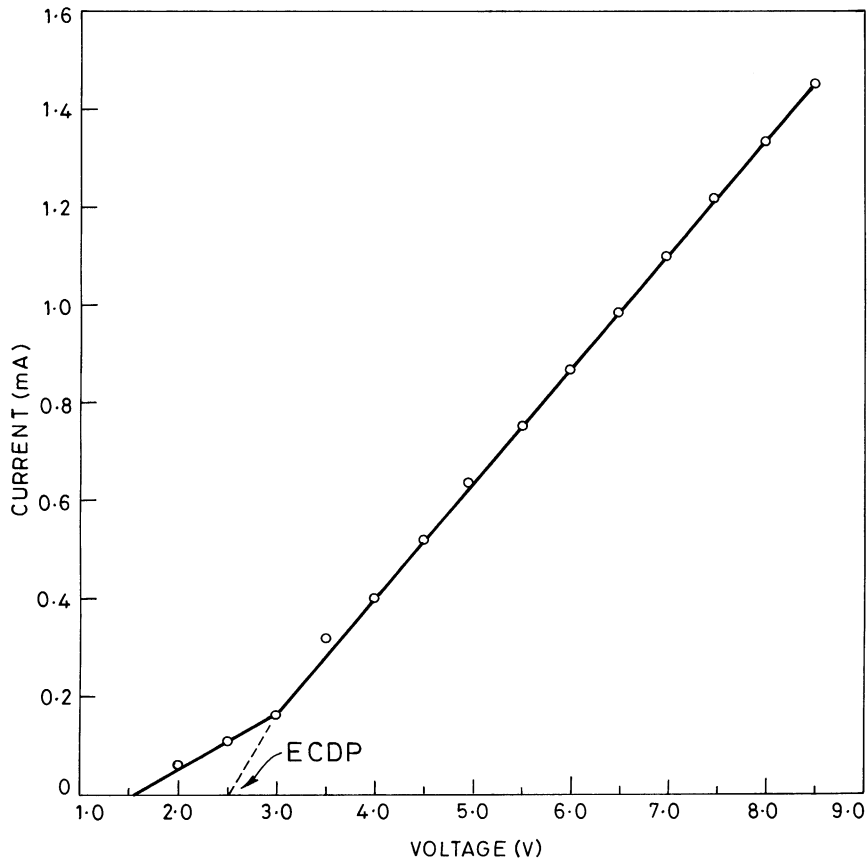


Fig. 5. Plot of applied voltage vs. current for determination of ECDP of (PVP + PVA + KIO₃) (35:35:30) polyblend electrolyte.

Table 4
Various cell parameters of (PVP + PVA + KIO₃) polyblend electrolyte

Cell parameters	(PVP + PVA + KIO ₃) (45:45:10)	(PVP + PVA + KIO ₃) (40:40:20)	(PVP + PVA + KIO ₃) (35:35:30)
Effective area of electrolyte (cm ²)	1.4	1.4	1.4
Cell weight (g)	1.90	1.86	1.60
Open-circuit voltage (V)	2.50	2.60	2.70
Short-circuit current (μA)	1200	1500	1800
Discharge time for plateau region (h)	160	168	176
Power density (mW kg ⁻¹)	19	16	26
Energy density (mWh kg ⁻¹)	3040	2688	4576
Current density (μA cm ⁻²)	857	1071	1286

Table 5
Comparison of present cell parameters with earlier reported data

Solid-state electrochemical cell configuration	Open-circuit voltage (V)	Short-circuit current (μA)	Discharge time for plateau region (h)	Reference
AgI(PEO + AgNO ₃)(I ₂ + C + electrolyte)	0.61	4.4	48	[17]
NaI(PEO + NaYF ₄)(I ₂ + C + electrolyte)	2.45	560	96	[11]
KI(PEO + KYF ₄)(I ₂ + C + electrolyte)	2.40	240	51	[11]
Na-HgI(PEO + NaPF ₆)(V ₂ O ₅ + C + electrolyte)	2.26	–	–	[10]
KI(PVP + PVA + KIO ₃)(I ₂ + C + electrolyte) (45:45:10)	2.50	1200	160	Present
KI(PVP + PVA + KIO ₃)(I ₂ + C + electrolyte) (40:40:20)	2.60	1500	168	Present
KI(PVP + PVA + KIO ₃)(I ₂ + C + electrolyte) (35:35:30)	2.70	1800	176	Present

4. Conclusions

The parameters of cells with (PVP + PVA + KIO₃) electrolyte films are comparable with those reported earlier for various other cells. This suggests a possible application of such cells as solid-state batteries. The observed open-circuit voltage of the cell is in good agreement with the electrochemical decomposition potential.

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