

Short communication

Effect of plasticizer on electrical conductivity and cell parameters of PVP + PVA + KClO₃ blend polymer electrolyte system

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Abstract

Solid polymer electrolyte films of polyvinylpyrrolidone (PVP), and poly(vinyl alcohol) (PVA) with KClO₃ and KClO₃ + plasticizer (dimethyl formamide) have been prepared by the solution - cast technique. Various experimental techniques such as electrical conductivity (composition dependence) at room temperature and transport number measurements are used to characterize these polymer electrolyte films. Electrochemical cells of configuration Kl(PVP + PVA + KClO₃)(I₂ + C + electrolyte) and Kl(PVP + PVA + KClO₃ + plasticizer)(I₂ + C + electrolyte) have been fabricated. The discharge characteristics of the cells are studied under a constant load of 100 kΩ. The open-circuit voltage, short-circuit current and discharge time for the plateau region are measured. The PVP + PVA + KClO₃ blend polymer electrolyte system with added plasticizer shows an increased discharge time with respect to the pure PVP + PVA + KClO₃ blend polymer electrolyte system.

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1. Introduction

Polymer materials are of present interest because, in combination with suitable metal salts, they give electrolytes which are useful for the development of advanced high-energy electrochemical devices, e.g. batteries, fuel cells, electrochemical display devices, smart windows, and photo electrochemical cells. The main advantages of polymeric electrolytes are their good mechanical properties, ease of fabrication into thin films of desirable sizes, and the ability to form good electrode/electrolyte contact. Most studies in this field are devoted to poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) based polymer electrolytes using alkali metal salts.

Several methods, such as copolymerisation, plasticization, blending and addition of ceramic fillers/additives, have been used to modulate the conductivity of the polymer electrolytes. Plasticizers are low molecular weight non-volatile substances (mostly liquids) which, when added to a polymer, improve its flexibility, processability and, hence, utility. The plasticizer substantially reduces the brittleness of many polymers because the addition of even small quantities

of the plasticizer markedly reduces the glass transition temperature, T_g , of the polymer. The electrical conductivity of a polymer electrolyte increases on the addition of plasticizer. The effect of the addition of plasticizer to polymer electrolytes and its effect on conductivity have been investigated by many workers [1–5].

In an attempt to investigate the possibilities of fabricating electrochemical cells based on polymers other than the widely studied polymers PEO, PPO, etc., this work reports the results obtained on a new polymer blend electrolyte polyvinylpyrrolidone (PVP) + PVA + KClO₃ and the effect of a plasticizer (dimethyl formamide) on its properties.

2. Experimental

Films (thickness: 150–200 μm) of pure PVP + PVA (50:50), PVP + PVA + KClO₃ (45:45:10; 40:40:20; 35:35:30) and PVP + PVA + KClO₃ + plasticizer (45:45:10; 40:40:20; 35:35:30) were prepared by the solution-cast technique using triple-distilled water as solvent. The mixture of these solutions was stirred for 10 h, cast on to polypropylene dishes, and evaporated slowly at room temperature. The final product was vacuum dried thoroughly at 10⁻³ m bar.

The dc conductivity was studied at room temperature as a function of composition using a conductivity cell designed

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in our laboratory [6]. The total ionic transport number (t_{ion}) was measured by means of Wagner's polarization technique [7]. In this technique, freshly prepared polymer electrolyte films are polarized in the configuration K/polymer blend electrolyte/C under a dc bias (step potential of 1.5 V). The resulting current was monitored as a function of time. After polarizing the electrolyte, the transport number t_{ion} was calculated from the initial current I_i and the final residual current I_{ele} , i.e.

$$t_{\text{ion}} = (I_i - I_{\text{ele}})/I_i$$

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

Using PVP + PVA + KClO₃ and PVP + PVA + KClO₃ + plasticizer polymer blends, electrochemical cells with configuration K|(PVP + PVA + KClO₃)(I₂ + C + electrolyte) and K|PVP + PVA + KClO₃ + plasticizer|(I₂ + C + electrolyte) were fabricated. The discharge characteristics of the cells were studied under a constant load of 100 kΩ. Details regarding the circuit and the diagram of the electrochemical cell are given elsewhere [8].

3. Results and discussion

The composition dependence of the dc conductivity of PVP + PVA + KClO₃ and PVP + PVA + KClO₃ + plasticizer polyblend electrolytes at room temperature is shown in Fig. 1, and the conductivity values are given in Table 1. The following features can be observed from the data.

The conductivity of a pure blend of PVP + PVA (50:50) is about $4.6 \times 10^{-7} \text{ S cm}^{-1}$ at room temperature. The change in conductivity with the composition of KClO₃ is small up to a composition of 20 wt.%, but thereafter increases significantly. With the addition of plasticizer, however, the con-

Table 1

Conductivity data of polymer electrolyte systems at room temperature

Polymer electrolyte (wt.%)	Conductivity (S cm ⁻¹)
PVP + PVA (50:50)	4.6×10^{-7}
PVP + PVA + KClO ₃ (45:45:10)	4.6×10^{-7}
PVP + PVA + KClO ₃ (45:45:10) + plasticizer	4.6×10^{-7}
PVP + PVA + KClO ₃ (40:40:20)	4.6×10^{-7}
PVP + PVA + KClO ₃ (40:40:20) + plasticizer	7.4×10^{-7}
PVP + PVA + KClO ₃ (35:35:30)	5.0×10^{-7}
PVP + PVA + KClO ₃ (35:35:30) + plasticizer	5.8×10^{-7}

ductivity is found to increase even from a 10 wt.% content of KClO₃. Plasticizer molecules being relatively small in size compared with polymer molecules penetrate the polymer matrix and establish attractive forces with the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, which enhances the conductivity and the discharge time.

Transport number measurements of the PVP + PVA + KClO₃ and PVP + PVA + KClO₃ + plasticizer electrolyte systems were evaluated by means of Wagner's polarization technique [7]. In this technique, the dc current is monitored as a function of time on application of a fixed dc voltage across the cell: K/polymer electrolyte/C. After polarization of the cell with 1.5 V dc, the current versus time plot is obtained, which is shown in Fig. 2 for the PVP + PVA + KClO₃ and PVP + PVA + KClO₃ + plasticizer electrolyte systems. The calculated transference numbers, t_{ion} and t_{ele} of the two electrolyte systems are given in Table 2. For all the compositions of the PVP + PVA + KClO₃ electrolyte systems, the values of the ionic transference numbers (t_{ion}) are in the range 0.92–0.95 and for the PVP + PVA + KClO₃ +

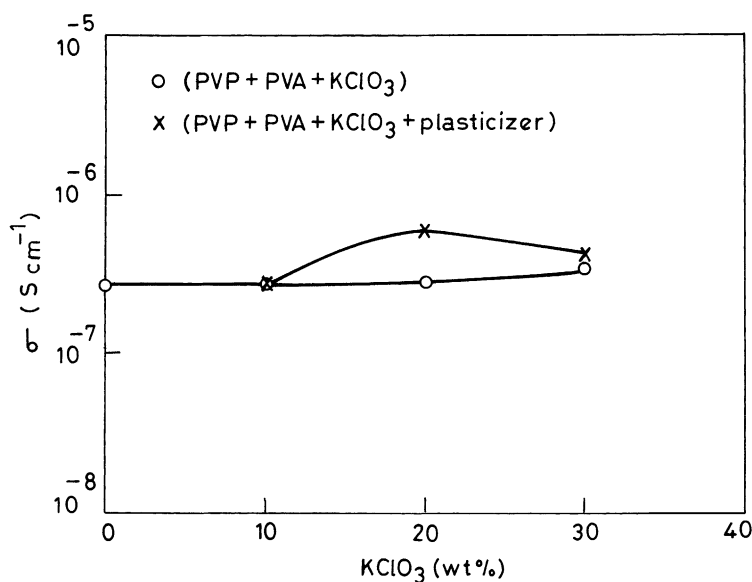


Fig. 1. Composition dependence of dc conductivity of (PVP + PVA + KClO₃) and (PVP + PVA + KClO₃ + plasticizer) polymer electrolyte system at room temperature.

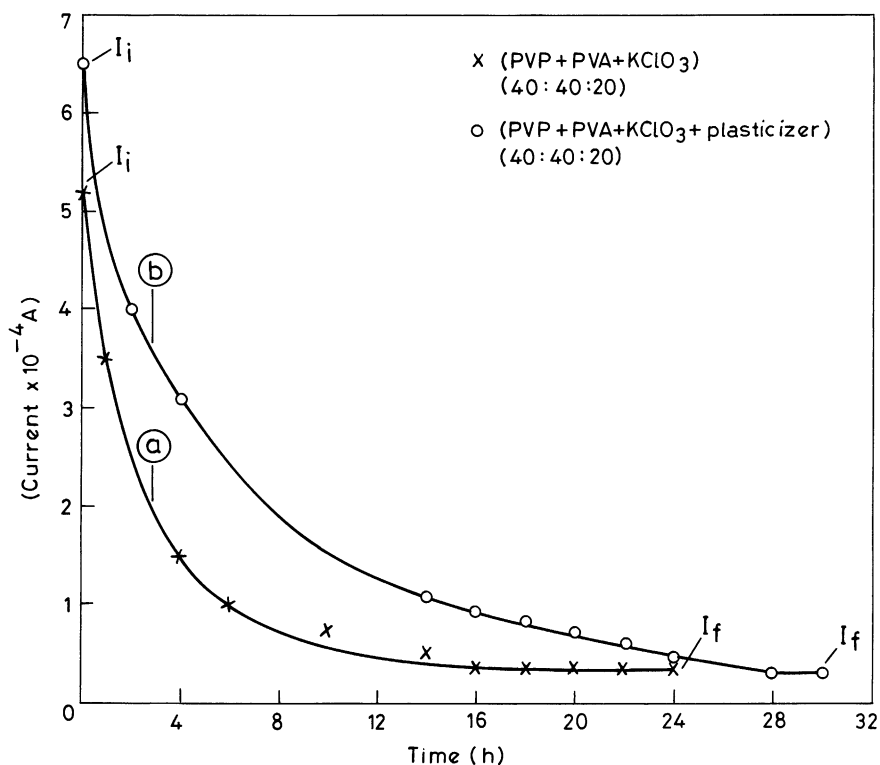


Fig. 2. Polarization current versus time plot for (a) PVP + PVA + KClO₃ (40:40:20) (b) PVP + PVA + KClO₃ (40:40:20) + plasticizer.

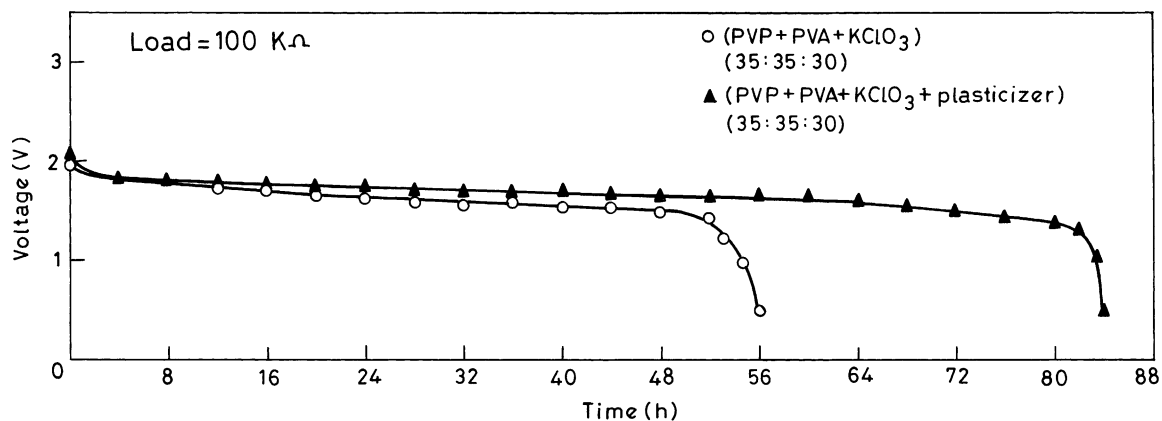


Fig. 3. Discharge characteristics of electrochemical cell K (anode)|(PVP + PVA + KClO₃) and PVP + PVA + KClO₃ + plasticizer|I₂ + C + electrolyte under a constant load of 100 kΩ.

Table 2

Transference numbers of PVP + PVA + KClO₃ and PVP + PVA + KClO₃ + plasticizer polymer electrolyte systems

Polymer electrolyte (wt.%)	Transference number	
	t_{ion}	t_{ele}
PVP + PVA + KClO ₃ (45:45:10)	0.95	0.05
PVP + PVA + KClO ₃ (45:45:10) + plasticizer	0.99	0.01
PVP + PVA + KClO ₃ (40:40:20)	0.93	0.07
PVP + PVA + KClO ₃ (40:40:20) + plasticizer	0.95	0.05
PVP + PVA + KClO ₃ (35:35:30)	0.92	0.08
PVP + PVA + KClO ₃ (35:35:30) + plasticizer	0.97	0.03

plasticizer electrolyte system are in the range 0.95–0.99. This suggests that the charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from the electrons. Using the polymer blend electrolytes, electrochemical cells were fabricated in the configurations K (anode)|(PVP + PVA + KClO₃ + plasticizer)|(I₂ + C + electrolyte) and K (anode)|(PVP + PVA + KClO₃)|(I₂ + C + electrolyte). The discharge characteristics of the electrochemical cells for a constant load of 100 kΩ are shown in Fig. 3. The initial sharp decrease in the voltage in these cells may be due to polarization and/or the formation of a thin layer of potassium salt at the electrode-electrolyte interface. The open-circuit voltage

Table 3
Cell parameters

Polymer electrolyte (wt.%)	Effective area of electrolyte (cm ²)	Cell weight (g)	Open-circuit voltage (V)	Short circuit current (μA)	Discharge time for plateau (h)	Current density (μA cm ⁻²)	Specific power (mW kg ⁻¹)	Specific energy (mWh kg ⁻¹)
PVP + PVA + KClO ₃ (45:45:10)	1.4	1.30	2.11	200	16	142.85	18.48	295.70
PVP + PVA + KClO ₃ (45:45:10) + plasticizer	1.4	1.45	2.26	290	34	207.14	16.57	563.34
PVP + PVA + KClO ₃ (40:40:20)	1.4	1.50	2.06	225	18	160.71	15.50	279.10
PVP + PVA + KClO ₃ (40:40:20) + plasticizer	1.4	1.30	2.26	270	36	192.86	17.31	623.10
PVP + PVA + KClO ₃ (35:35:30)	1.4	1.30	2.00	521	52	372.14	22.23	1156.00
PVP + PVA + KClO ₃ (35:35:30) + plasticizer	1.4	1.30	2.07	600	82	428.57	20.31	1665.42

and short-circuit current of the PVP + PVA + KClO₃ (35:35:30) + plasticizer cell are 2.07 V and 600 μA, and for the PVP + PVA + KClO₃ (35:35:30) cell are 2.0 V and 521 μA, respectively. The other parameters for these cells were evaluated and are listed in Table 3. The data indicate that the cell parameters are better in the cell with the plasticizer. This suggests that plasticized polymer electrolyte cells exhibit improved performance and better stability than pure polymer counterparts. Plasticizer polymer electrolytes thus offer an interesting alternative to other reported electrolyte systems for room temperature solid-state batteries.

4. Conclusions

Parameters are evaluated for pure and plasticizer-added PVP + PVA + KClO₃ polymer electrolyte cells. The plasticized cells exhibit better performance, which indicates that such cells are more suitable for fabricating solid-state batteries.

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