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Short communication

Study of transport and electrochemical cell characteristics of PVP:$NaClO_3$ polymer electrolyte system

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Abstract

A solid polymer electrolyte system based on poly(vinyl pyrrolidone) (PVP) complexed with sodium chlorite ($NaClO_3$) salt has been prepared by a solution — cast technique. Several experimental techniques, such as composition-dependence conductvity, temperature-dependence conductivity in the temperature range of 303–398 K and transport number measurements, have been employed to characterize this polymer electrolyte system. The conductivity of the (PVP + $NaClO_3$) electrolyte is about 10^4 times larger than that of pure PVP at room temperature. Transport number measurements show that the charge transport is mainly due to ions. An electrochemical cell with the configuration Na/(PVP + $NaClO_3$)/(I_2 + C + electrolyte) has been fabricated and its discharge characteristics studied. The open-circuit voltage and short-circuit current are 2.77 V and 1.35 mA, respectively. A number of other cell parameters are reported.

Keywords: Ionic conductivity; Polymer electrolyte; Transport number; Electrochemical cell; Sodium chlorite

1. Introduction

Polymer materials in combination with suitable metal salts give electrolytes for advanced, high energy electrochemical devices, e.g. batteries/fuel cells, electrochemical display devices/smart windows, and photo-electrochemical cells [1–5]. The main advantages of polymeric electrolytes are satisfactory mechanical properties, ease of fabrication as thin-films, and an ability to form good electrode/electrolyte contact. Most of the studies in this field are devoted to polyethylene oxide (PEO) and polypropylene oxide (PPO)-based polymer electrolytes using alkali metal salts [6–11]. Some proton-conducting polymer electrolytes have been reported based on PEO complexed with ammonium salts such as NH_4SCN [12], $NH_4SO_3CF_3$ [12], NH_4ClO_4 [13,14], and NH_4I [15].

In an attempt to investigate the possibility of fabricating electrochemical cells based on other polymers, studies have been conducted on electrochemical cells based on poly(acrylamide) (PA) and poly(vinyl pyrrolidone) (PVP) polymers [16–19]. The present work examines a new polymer electrolyte, namely (PVP + $NaClO_3$). Using this electrolyte, an electrochemical cell has been fabricated and its discharge characteristics studied.

2. Experimental

Films (thickness, 150–200 μm) of pure PVP (molecular weight, 4×10^4) and various compositions of complexed films of PVP with sodium chlorite ($NaClO_3$) were prepared in the weight ratios (90:10), (80:20) and (70:30) by a solution — cast technique. Aqueous solutions of PVP and $NaClO_3$ mixtures were stirred for 10–12 h. The stirred solution was cast on to polypropylene dishes and evaporated slowly at room temperature. The final product was vacuum dried thoroughly at 10^{-3} Torr.

The dc conductivity was measured, using an in-house conductivity instrument [10], in the temperature range of 303–398 K. The ionic and electronic transport numbers (t_{ion} and t_{ele}) were evaluated by means of Wagner's polarization technique [20]. In this technique, a freshly prepared film of (PVP + $NaClO_3$) was polarized with a configuration of Na/(PVP + $NaClO_3$)/C under a dc bias (step potential, 1.5 V). The resulting current was monitored as a function of time with a Keithly electrometer (model 614).

An electrochemical cell was fabricated with the configuration Na/(PVP + $NaClO_3$)/(I_2 + C + electrolyte). The

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details regarding the fabrication of such cells are given, elsewhere [21]. The discharge characteristics of the cell were monitored under a constant load of 100 kΩ.

3. Results and discussion

The variation in dc conductivity (σ) as a function of $NaClO_3$ composition in PVP at various temperatures is given in Fig. 1. Conductivity data at room temperature are reported in Table 1. The following conclusions can be drawn.

The conductivity of pure PVP is $\sim 10^{-11}$ S cm^{-1} at room temperature and its value increases sharply to $\sim 10^{-7}$ S cm^{-1} on complexing with 10 wt.% $NaClO_3$. The increase in conductivity becomes slower on further addition of $NaClO_3$ to the polymer. This behavior has been explained by various researchers, who have studied PVP- and PEO-based polymer electrolyte, in terms of ion association and the formation of charge multiples [19,22–24].

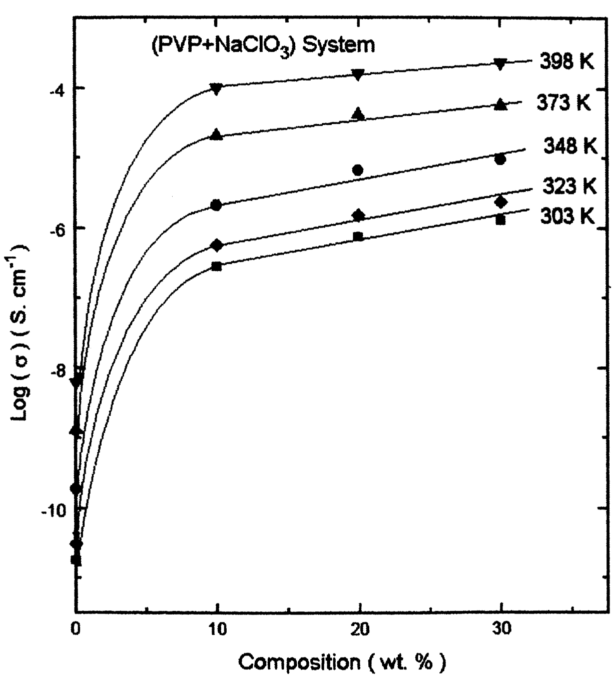

Fig. 1. Composition vs. conductivity plots of ($PVP + NaClO_3$) polymer electrolyte system.

Table 1
Conductivity and transport number data for ($PVP + NaClO_3$) electrolyte system

Sample	Direct current-conductivity at 303 K (S m^{-1})	Transport number	
		t_{ion}	t_{ele}
PVP	1.78×10^{-11}	–	–
PVP + $NaClO_3$ (90:10)	2.81×10^{-7}	0.95	0.05
PVP + $NaClO_3$ (80:20)	3.03×10^{-7}	0.97	0.03
PVP + $NaClO_3$ (70:30)	3.28×10^{-7}	0.99	0.01

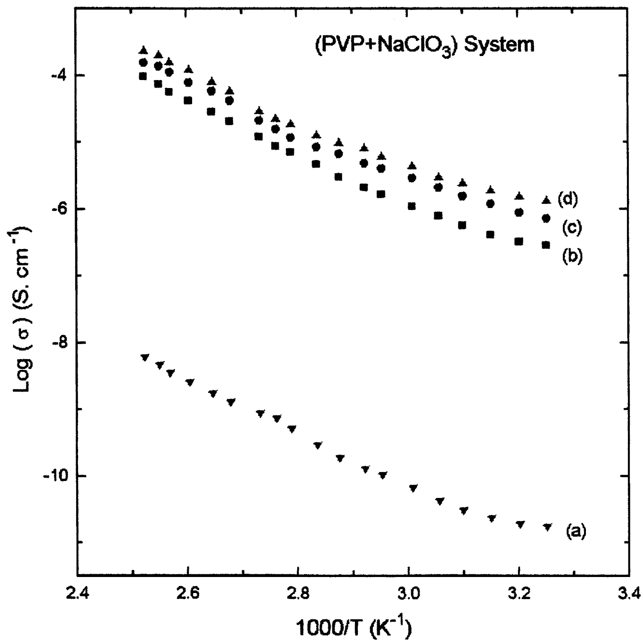

Fig. 2. Temperature-dependent conductivity of: (a) pure PVP; (b) ($PVP + NaClO_3$) (90:10); (c) ($PVP + NaClO_3$) (80:20); (d) ($PVP + NaClO_3$) (70:30).

The variation in conductivity as a function of temperature for pure PVP and for different compositions of ($PVP + NaClO_3$) polymer electrolyte over the temperature range of 303–398 K is shown in Fig. 2. The conductivity increases with temperature in pure PVP and in all the

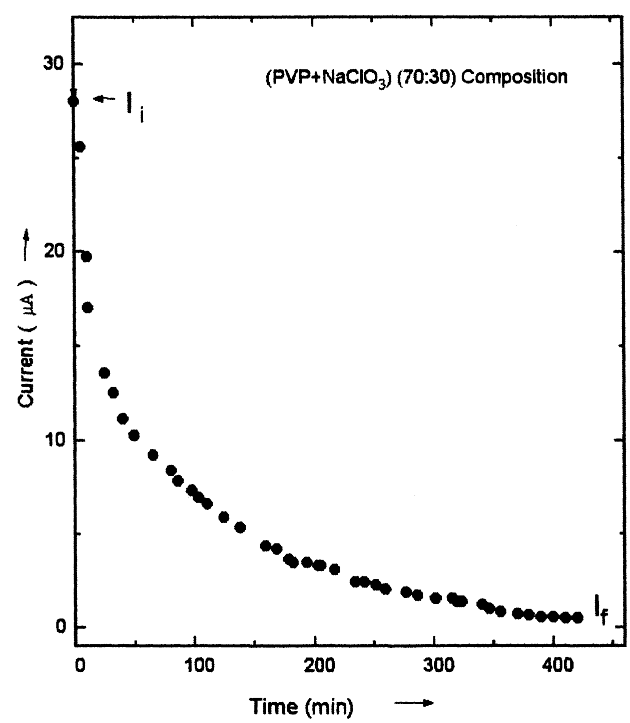

Fig. 3. Current vs. time plot of ($PVP + NaClO_3$) (70:30) polymer electrolyte film.

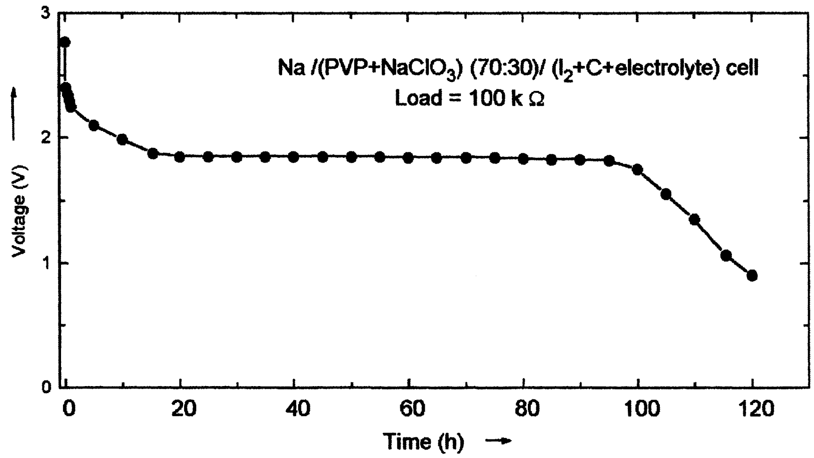

Fig. 4. Discharge characteristics of a Na/(PVP + $NaClO_3$) (70:30)/(I_2 + C + electrolyte) cell.

compositions of the (PVP + $NaClO_3$) polymer electrolyte system. The ionic conductivity in the polymer complexes may be interpreted on the basis of a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer chains; these are essential to assure high conductivity of the electrolyte [19,25–27].

The current versus time graph following polarization of the cell with 1.5 V dc is shown in Fig. 3. The transference numbers and (t_{ion} and t_{ele}) have been calculated from this plot using the following 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 the final residual current. The resulting data are given in Table 1. For all the compositions of the (PVP + $NaClO_3$) electrolyte system, the values of the ionic transference numbers t_{ion} are in the range of 0.95–0.99. This suggests that the charge transport in these polymer electrolyte films is mainly due to ions; only a negligible contribution comes from the electrons.

The discharge characteristics of the cell Na/(PVP + $NaClO_3$) (70:30)/(I_2 + C + electrolyte) at an ambient temperature for a constant load of 100 kΩ are shown in Fig. 4. The initial sharp decrease in the voltage and current in these cells may be due to polarization and/or to the formation of a thin layer of sodium salt at the electrode electrolyte interface. The open-circuit voltage (OCV) and short-circuit current (SCC) of these cells are 2 77 V and 1.35 mA, respectively. The various other cell parameters are: cell weight, 958 mg; area of the cell, 1.34 cm^2; discharge time for plateau region, 104 h; specific power, 35.7 mW kg^{-1}; specific energy, 3712.8 mWh kg^{-1}.

On the basis of present study, a so1id-state battery with (PVP + $NaClO_3$) as electrolyte is promising. Further work aimed at obtaining higher cell capacities and specific energy is in progress.

4. Conclusions

The charge transport in these polymer electrolytes (PVP + $NaClO_3$) is mainly due to ions The open-circuit voltage and short-circuit current for a cell with the configuration Na/(PVP + $NaClO_3$)/(I_2 + C + electrolyte) are 2.77 V and 1.35 mA, respectively.

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