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Ion transport and electrochemical cell characteristic studies of a new (PVP + $NaNO_3$) polymer electrolyte system

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Polymer electrolyte films based on poly (vinyl pyrrolidone) (PVP) complexed with $NaNO_3$ salt have been prepared by solution—cast technique. Several experimental techniques such as X-ray diffraction, Infrared (IR), DC—electrical conductivity, transference number measurements have been employed to characterize the polymer electrolyte. The conductivity of the (PVP + $NaNO_3$) electrolyte is about 10^4 times larger than that of pure PVP at room temperature. The transference number measurements show that the charge transport in this polymer electrolyte system is predominantly due to ions. Using this polymer electrolyte, an electrochemical cell with the configuration Na/(PVP + $NaNO_3$)/(I_2 + C + electrolyte) has been fabricated and its discharge characteristics studied. The open circuit voltage (OCV) and short circuit current (SCC) observed for the cell are 2.65 V and 1.1 mA respectively. A number of other cell parameters evaluated are also reported.

1. Introduction

In recent years, substantial interest has been devoted to polymer materials, which in combination with suitable metal salts, give electrolytes of the development of advanced high energy electrochemical devices, e.g., batteries/fuel cells, electrochemical display devices/smart windows, photo electrochemical cells, etc. [1–5]. The main advantages of polymeric electrolytes are their mechanical properties, ease of fabrication of thin films of desirable sizes and their ability to form proper electrode/electrolyte contact. Most of the studies in this field are devoted to PEO-based polymer electrolytes using alkali salts, e.g., $LiBF_4$, $LiPF_6$ and $LiB(C_6H_5)_4$ [6], LiSCN [7], $LiSO_3CF_3$ and $LiClO_4$ [8], NaSCN [9], $NaYF_4$ [10], KYF_4 [11], etc. Some PEO-based polymer electrolytes are also reported with salts of divalent and transition metal cations such as halides of Zn, Cd, Mg, Pb, Cu, Fe, Ni, Co [12–14]. Some proton conducting polymer electrolytes have been reported based on PEO complexed with ammonium salts such as NH_4SCN and $NH_4SO_3CF_3$ [15], NH_4ClO_4 [16, 17], NH_4I [18].

In an attempt to investigate the possibility of fabricating electrochemical cells based on polymers other than widely studied polymers PEO, PPO, etc., the authors have reported the results obtained on electrochemical cells based on poly (acrylamide) (PA) and poly (vinyl pyrrolidone) (PVP) polymers [19–21]. In the present paper, the authors report the results obtained on a new polymer electrolyte (PVP + $NaNO_3$). Using this electrolyte, an electrochemical cell has been fabricated and its discharge characteristics studied.

2. Experimental

Films (thickness: 150 to 200 μm) of pure PVP (M.W. 4×10^4) and various compositions of complexed films of PVP with $NaNO_3$ were prepared in the weight ratios (90 : 10), (80 : 20) and (70 : 30) by a solution-cast technique. Aqueous solutions of PVP and $NaNO_3$ mixtures were stirred for 10–12 hours. The stirred solution was cast onto polypropylene dishes and evaporated slowly at room temperature. The final product was vacuum dried thoroughly at 0.13 Pa.

The XRD spectra of all the films were obtained by means of a SEIFERT X-ray diffractometer in the range $2\theta = 5$ to 50°. The IR spectra of the films were recorded with the help of Perkin Elmer FT-IR spectrophotometer [Model 1605] in the range of 450 to 4500 cm^{-1}. The d.c. conductivity was measured using the lab made conductivity instrument [10], in the temperature range of 303 to 373 K. The ionic and electronic transport numbers (t_{ion} and t_{ele}) were evaluated by means of the Wagner's polarization technique [22]. In this technique, a freshly preaped film of (PVP + $NaNO_3$) was polarized with a configuration of Na/(PVP + $NaNO_3$)/C under a d.c. bias (step potential of 1.5 V). The resulting current was monitored as a function of time with a Keithly electrometer [Model 614].

Further, an electrochemical cell was fabricated with the configuration Na/(PVP + $NaNO_3$)/(I_2 + C + electrolyte). The details regarding the fabrication of the electrochemical cells are given elsewhere [23]. Sodium metal was used as anode and the cathode material was a composite electrode by mixing iodine, graphite and electrolyte in the ratio (5 : 5 : 1). The discharge characteristics of the cell were monitored under a constant load of 100 kΩ.

3. Results and discussion

The complexation of PEO and PVP with various salts has been studied using X-ray diffraction and vibrational spectroscopic analysis [10, 11, 16–21, 23, 24]. The XRD patterns of pure $NaNO_3$, pure PVP and PVP + $NaNO_3$ systems are given in Fig. 1. A comparison of the spectra of (PVP + $NaNO_3$) films with that of pure PVP and $NaNO_3$ reveals the following differences.

Well-defined sharp peaks were observed in pure $NaNO_3$, indicating its crystalline nature. In the case of pure PVP, no such well-defined peaks were observed. Instead, a broad peak was observed at $2\theta = 13^\circ$, suggesting the multiphase system having crystalline and amorphous nature of these films. With the addition of $NaNO_3$ to PVP, no well-defined peaks were observed. A broad peak appeared in PVP was suppressed in $NaNO_3$ added PVP polymer films. This suggests that the PVP + $NaNO_3$ polymer electrolyte films have amorphous nature. No peaks corresponding to $NaNO_3$ are observed in the PVP + $NaNO_3$ electrolyte films, indicating the absence of excess salt in the material.

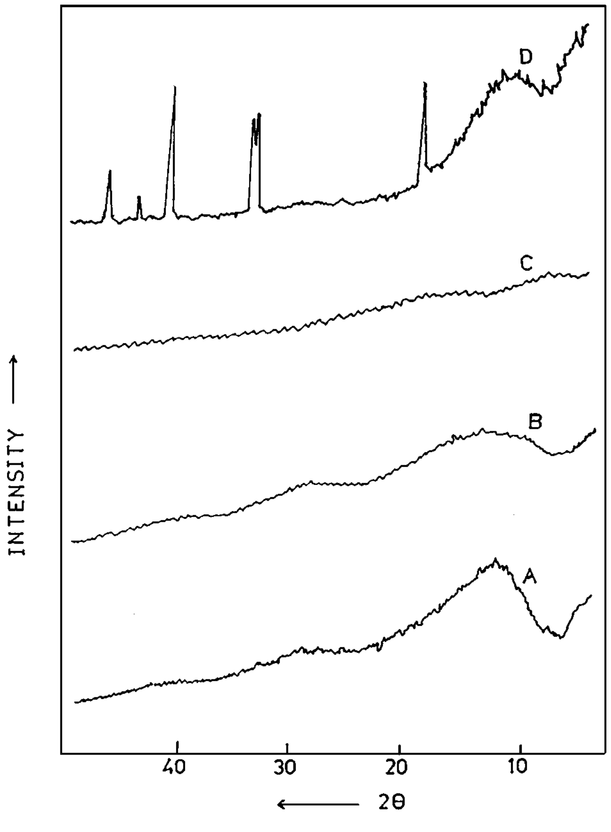

Figure 1 X-ray diffraction spectra of (A) PVP, (B) (PVP + $NaNO_3$) (90 : 10), (C) (PVP + $NaNO_3$) (70 : 30) and (D) $NaNO_3$.

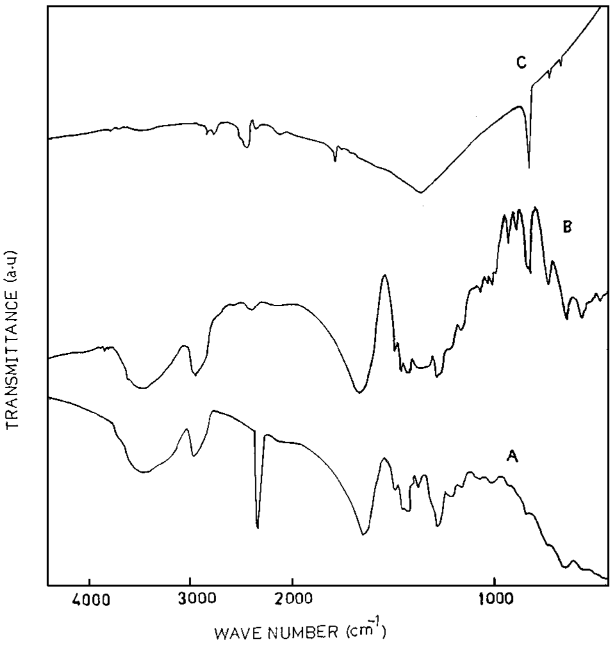

Figure 2 IR-Spectra of (A) PVP, (B) (PVP + $NaNO_3$) (70 : 30) and (C) $NaNO_3$.

Fig. 2 shows the IR spectra taken for PVP, (PVP + $NaNO_3$) (70 : 30) composition and $NaNO_3$. When the IR spectra of (PVP + $NaNO_3$) is compared with that of pure PVP and $NaNO_3$, the following changes have been observed.

A sharp dominant peak observed in PVP at 2359.9 cm^{-1} disappeared in (PVP + $NaNO_3$) spectra. A number of peaks corresponding to PVP and $NaNO_3$ were shifted in (PVP + $NaNO_3$), due to the addition of the salt in the polymer. The shifting and disappearing of peaks in the IR spectra of (PVP + $NaNO_3$) clearly indicate the complex between the salt and the polymer.

Thus, the results of XRD and IR data for these films clearly confirm the formation of complexes between the $NaNO_3$ and the PVP polymer.

The variation in d.c conductivity, σ, as a function of the $NaNO_3$ composition in PVP at various temperatures is given in Fig. 3. The conductivity data at RT are given in Table I. The following conclusions can be drawn.

The conductivity of pure PVP is $\sim 10^{-13}$ $S \cdot m^{-1}$ at room temperature and its value increases sharply to $\sim 10^{-9}$ $S \cdot m^{-1}$ on complexing with 10 wt.% $NaNO_3$. The increase in conductivity becomes slower on further addition of $NaNO_3$ salt to the polymer, this may be explained on the basis of ion association and charge multiplets formation. This nature of conductivity has been explained by various researchers on PEO based polymer electrolytes using the concept of ion association and charge multiplets formation [25, 26].

In general, it is believed that the conductivity increases as the degree of amorphous phase increase. The continuous increase in conductivity in the present study of the (PVP + $NaNO_3$) system with increasing $NaNO_3$ salt concentration is attributed the increase in amorphous phase as observed by XRD analysis.

TABLE I Conductivity, activation energy and transport number data of PVP and (PVP+$NaNO_3$) electrolyte system

Sample	DC-conductivity (303 K) ($S{\cdot}m^{-1}$)	Activation energy E_a(eV)	Transport numbers t_{ion}	t_{ele}
Pure PVP	4.164×10^{-13}	0.35	—	—
PVP + $NaNO_3$ (90 : 10)	4.01×10^{-9}	0.71	0.89	0.11
PVP + $NaNO_3$ (80 : 20)	7.220×10^{-9}	0.73	0.91	0.09
PVP + $NaNO_3$ (70 : 30)	9.195×10^{-9}	0.79	0.93	0.07

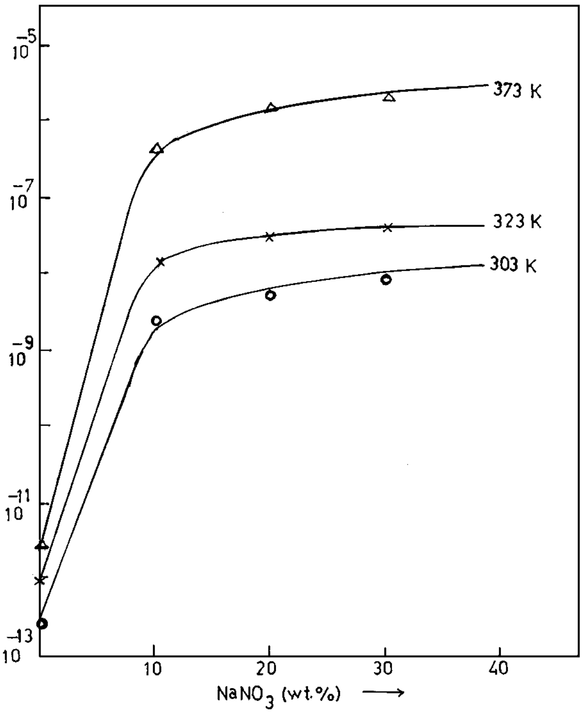

Figure 3 Composition vs. conductivity plots of (PVP + $NaNO_3$) polymer electrolyte system at different temperatures.

The variation of conductivity as a function of temperature for pure PVP and for different compositions of (PVP + $NaNO_3$) polymer electrolyte over the temperature range 303 to 373 K is shown in Fig. 4. From Fig. 4, the conductivity increases with temperature in pure PVP and also in all the compositions of the (PVP + $NaNO_3$) 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 to the electrolyte [27–29].

The variation of conductivity of pure PVP and different compositions of the (PVP + $NaNO_3$) electrolyte system was found to follow the Arrhenius relation

$$\sigma = \left(\frac{\sigma_0}{T}\right) \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

where σ_0 is the pre-exponential factor, T is the absolute temperature, k is the Boltzmann constant and E_a is the activation energy. The activation energies are given in Table I, for pure PVP and (PVP + $NaNO_3$) polymer electrolyte systems.

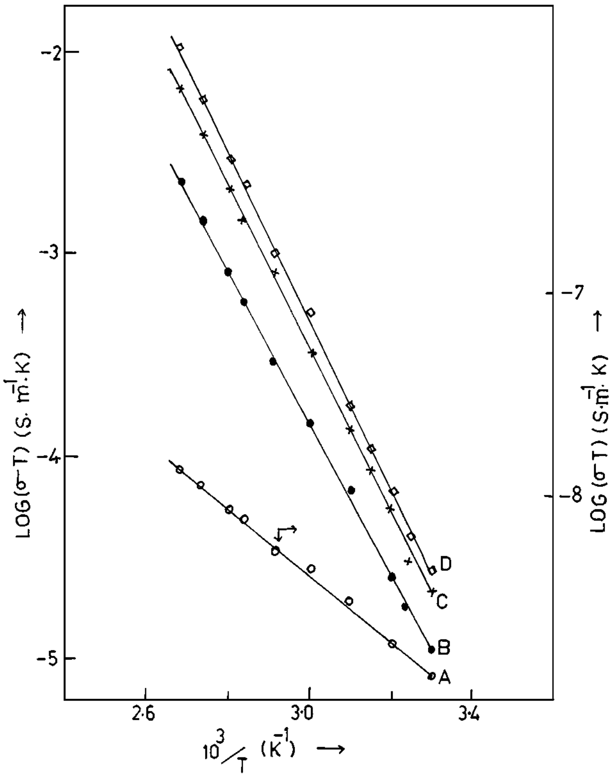

Figure 4 Temperature dependent conductivity of: (A) pure PVP, (B) (PVP + $NaNO_3$) (90 : 10) (C) (PVP + $NaNO_3$) (80 : 20) and (D) (PVP + $NaNO_3$) (70 : 30).

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) of the (PVP + $NaNO_3$) system have been evaluated using Wagner's polarization technique [22]. In this method the dc-current was monitored as a function of time on application of a fixed dc voltage across the cell Na/(PVP + $NaNO_3$)/C. After polarization of the cell with 1.5 V dc the current versus time graph is shown in Fig. 5. The transference numbers (t_{ion} and t_{ele}) have been calculated from the polarization curent versus time plot using the equations:

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

$$t_{ele} = \frac{I_f}{I_i} \quad (3)$$

where I_i is the initial current and I_f is the final residual current. The resulting data are given in Table I, for all the compositions of the (PVP + $NaNO_3$) electrolyte system, the values of the ionic transference numbers t_{ion} are in the range 0.89 to 0.93. This suggest that the charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from the electrons.

Using this polymer electrolyte the electrochemical cell has been fabricated with the configuration Na/(PVP + $NaNO_3$)/(I_2 + C + electrolyte). Fig. 6 shows the discharge characteristics of the cell Na/(PVP + $NaNO_3$) (70 : 30)/(I_2 + C + electrolyte) at an

TABLE II Comparison of cell parameters of various polymer electrochemical cells

Electrochemical cell with configuration	Open circuit voltage (OCV) (V)	Short circuit current (SCC) (μA)	Time for plateau region (h)	References
Ag/(PVP + $AgNO_3$)/(I_2 + C + Electrolyte)	0.46	65	82	[20]
Ag/(PEO + $AgNO_3$)/(I_2 + C + Electrolyte)	0.610	4.4	48	[24]
Na/(PEO + $NaYF_4$)/(I_2 + C + Electrolyte)	2.45	560	96	[10]
Na/(PVP + $NaNO_3$)/(I_2 + C + Electrolyte)	2.65	1100	90	Present

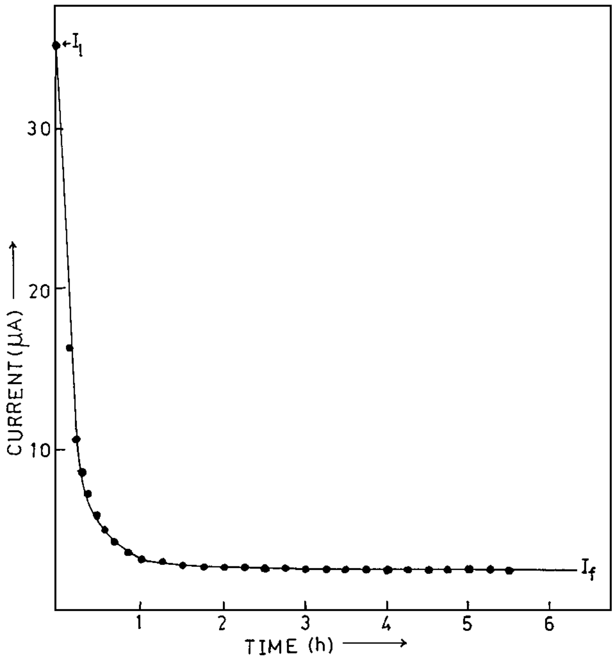

Figure 5 Current vs. time plot of (PVP + $NaNO_3$) (70 : 30) polymer electrolyte.

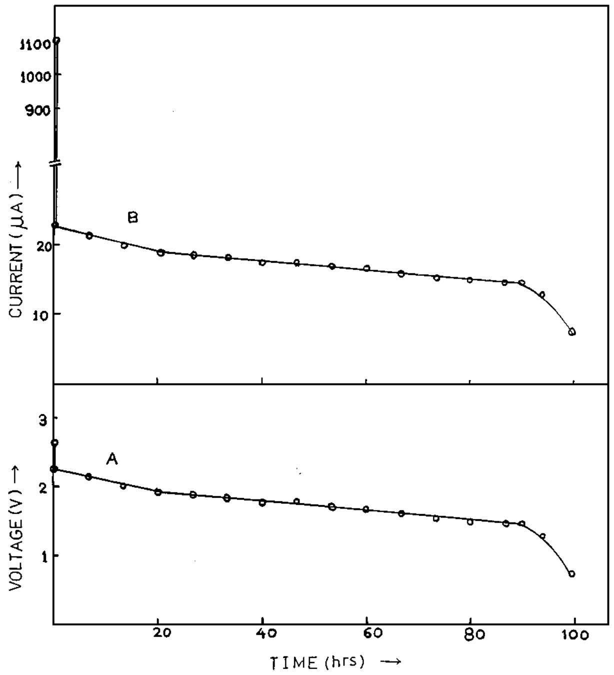

Figure 6 (A & B). Discharge characteristics of the electrochemical cell Na/(PVP + $NaNO_3$) (70 : 30)/(I_2 + C + electrolyte) under a constant load of 100 kΩ.

ambient temperature for a constant load of 100 kΩ. The initial sharp decrease in the voltage and current in these cells may be because of the polarization and/or 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 have been determined which are 2.65 volts and 1.1 mA respectively. The various other cell parameters are summarized below:

Cell weight = 800 mg

Area of the cell = 134 mm^2

Discharge time for plateau region = 90 h

Power density = 0.384 W/kg and

Energy density = 34.56W-h/kg.

For comparison, the cell parameters obtained for PVP based electrolytes along with PEO based cells are given in Table II [10, 20, 24]. From the comparison, it is clear that the sodium based polymer electrolyte cells show better cell performance compared to the silver based polymer electrolyte cells. Further, the PVP based polymer electrolytes also showed comparable cell characteristics with these of PEO based electrolytes.

On the basis of present study the solid state battery with (PVP + $NaNO_3$) as electrolyte provides a good option. Further work in the direction of obtaining higher cell capacities and energy density in progress.

4. Conclusions

The charge transport in these polymer electrolytes (PVP + $NaNO_3$) is predominantly due to ions. The open circuit voltage (OCV) and short circuit current (SCC) obtained for the electrochemical cell with the configuration Na/(PVP + $NaNO_3$)/(I_2 + C + electrolyte) were found to be 2.65 V and 1.1 mA respectively.

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