

Ion conducting polymer electrolyte films based on (PVP+NaF) system and its application as an electrochemical cell

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Abstract - A sodium ion-conducting polymer electrolyte based on Polyvinyl pyrrolidone (PVP, $M_w=4 \times 10^4$) complexed with NaF was prepared using the solution-cast technique. The features of the complexation of the electrolytes were studied by X-ray diffraction (XRD) and FTIR techniques. The ionic conductivity and transference number measurements were performed to characterize the polymer electrolyte for battery applications. 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 $\text{Na} / (\text{PVP}+\text{NaF}) / (\text{I}_2+\text{C}+\text{electrolyte})$ has been fabricated and its discharge characteristics were studied.

Key Words: XRD, FTIR, AC conductivity, transference numbers, discharge profiles

1. INTRODUCTION

In the recent years, polymer materials in combination with suitable metal salts give electrolytes for advanced high energy electrochemical devices such as batteries/fuel cells, electrochemical display devices/smart windows and photoelectrochemical cells, etc. [1, 2]. 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 poly (ethylene oxide) (PEO) and poly (propylene oxide) (PPO) based polymer electrolytes using alkali metal salts [3, 4]. In an attempt to study the possibility of fabricating electrochemical cells based on polymers other than widely studied polymers such as PEO, PPO etc., studies have been undertaken on electrochemical cells based on poly (acrylamide) (PA) and poly (vinyl pyrrolidone) (PVP) polymers [5].

The present work is concerned with solid-state electrochemical cells which are based on (PVP+NaF)

electrolyte films. Several experimental techniques such as XRD, FTIR, electrical, transference numbers and discharge profiles were performed to characterize these plasticized polymer blend electrolytes.

2. EXPERIMENTAL

Films (thickness $\sim 150 \mu\text{m}$) of pure PVP and various compositions of complexed films of PVP with NaF salt were prepared with weight percent ratios (90:10), (80:20) and (70:30) by a solution-cast technique using methanol (water-free) as solvent. 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 XRD patterns of the films were made with a SEIFERT X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.540 \text{ \AA}$) in the range 10° - 70° . The infrared spectra of the films were recorded on a Perkin-Elmer FTIR spectrophotometer [Model 1605] in the range 4000 cm^{-1} - 400 cm^{-1} . The ac impedance measurements of the polymer electrolytes were performed using a computer controlled phase sensitive multimeter (PSM 1700) in the frequency range 1 Hz - 1MHz and in the temperature range of 303 - 373 K. The total ionic transport number (t_{ion}) was evaluated by means of Wagner's polarization technique [6]. Solid-state electrochemical cells were fabricated with a configuration of $\text{Na}/(\text{PVP}+\text{NaF})/(\text{I}_2+\text{C}+\text{electrolyte})$. Details of the fabrication of the electrochemical cell are given elsewhere [7]. The discharge characteristics of the cells were monitored under a constant load of 100 k Ω .

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction studies

In order to investigate the complexation of sodium fluoride salt with the polymer electrolyte, XRD studies were performed. Fig 1 shows the comparative profiles of the XRD patterns of Pure PVP film, NaF salt and the complexed (PVP+NaF) films with different wt% ratios (90:10), (80:20) and (70:30).

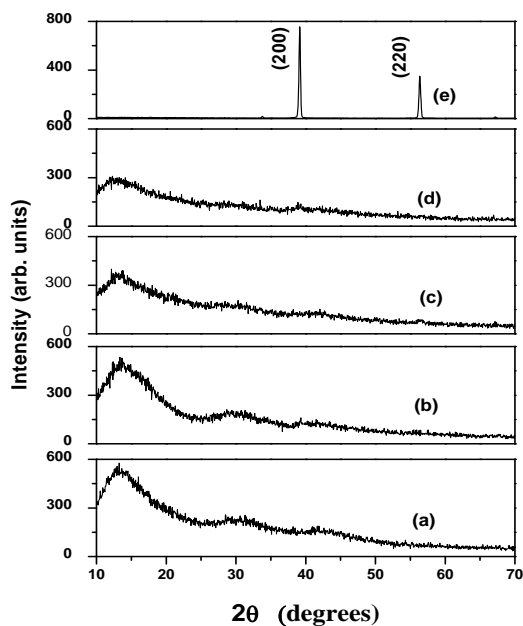


Fig - 1: XRD patterns of (a) Pure PVP (b) PVP+NaF (90:10) (c) PVP+NaF (80:20) (d) PVP+NaF (70:30) polymer films and (e) NaF salt

A comparison of the diffraction spectra of complexed PVP with that of pure PVP and NaF reveals the following differences.

- Two broad amorphous humps are observed for 2θ values at around 13° and 29.3° , were found to be less intense in complexed PVP films compared to the pure PVP film. This indicated that the addition of NaF salt caused a decrease in the degree of crystallinity of the PVP. This could be due to the disruption of the semi-crystalline structure of the film by NaF salt. Hodge et al [8] established a correlation between the intensity of the peak and the degree of crystallinity.
- No peaks corresponding to NaF were observed in complexed PVP, indicating the absence of excess salt (uncomplexed) in the complexed polymer films.
- The humps exhibited a decrease in intensity with broadening at higher concentrations of NaF salt in the polymer. This indicated a continuous decrease in the crystalline phase and a dominant presence of the amorphous phase. This amorphous nature results in greater ionic diffusivity with high ionic conductivity, as amorphous polymers have flexible backbone [9].

3.2 IR Spectra

The IR spectra of pure PVP, NaF and NaF complexed with PVP are shown in Fig-2. The following differences in the spectral features have been observed on comparing the spectra of complexed PVP with pure PVP and NaF.

- A vibration band observed around 2950 cm^{-1} may be attributed to C-H stretching of PVP. The intensity of the band decreases by the addition of NaF salt.

- The bands appearing in the $1708 - 1620\text{ cm}^{-1}$ region in all films correspond to symmetric and asymmetric of C=O stretching modes of PVP.
- CH_2 bending mode exhibited at around 1488 cm^{-1} is shifted to $1474, 1460$ and 1458 cm^{-1} in 10, 20 and 30 wt% NaF salt complexed films, respectively. This decrease in the wave number results in the increase in band length indicating complexation.
- The band at 1435 cm^{-1} corresponding to CH_2 wagging mode shifts towards the lower wavenumbers with the increase of dopant concentration.
- The bands around 1018 and 874 cm^{-1} correspond to C-C stretching and CH_2 rocking modes of PVP. A small sharp peak appears at 739 cm^{-1} which is assigned to C-N stretching of PVP.
- The appearance of new peaks along with changes in the existing peaks and/or their disappearance in the IR spectra directly indicate the complexation of NaF with PVP.
- The characteristic bands around $1177, 1293, 1378$ and 1395 cm^{-1} of PVP get shifted with the addition of NaF.

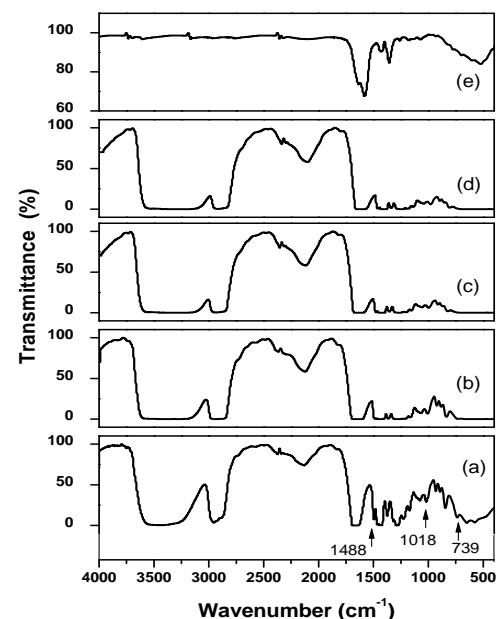


Fig - 2: IR spectra of (a) Pure PVP (b) PVP+NaF (90:10) (c) PVP+NaF (80:20) (d) PVP+NaF (70:30) (e) NaF salt

3.3 AC impedance studies

Typical impedance plots (Z' vs Z'') for PVP and (PVP+NaF) composite electrolytes at different temperatures are shown in Fig-3, which showed a normal impedance behaviour such as a depressed semicircular portion followed by a spike (residual tail). In the complex impedance representation, the low frequency response appears as an inclined spike and such a spike (tail-like) is characteristic of a blocking double-layer capacitance. The

high frequency semicircle corresponds to the bulk response of the films. These results suggest that the migration of ions may occur through the volume of matrix polymer, which can be represented by a resistor. The immobile polymer chains, on the other hand, become polarized in the alternating field, and can therefore be represented by a capacitor. The ionic migration and bulk polarization are physically in parallel, and therefore, the portion of the semicircle can be observed at high frequencies [10]. The ionic conductivity of PVP and (PVP+NaF) polymer electrolytes is calculated from the relation

$$\sigma = I/R_b A \quad (3)$$

where I, the thickness of the film, A, the area of the film and R_b , the bulk resistance of the material which is obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance [11].

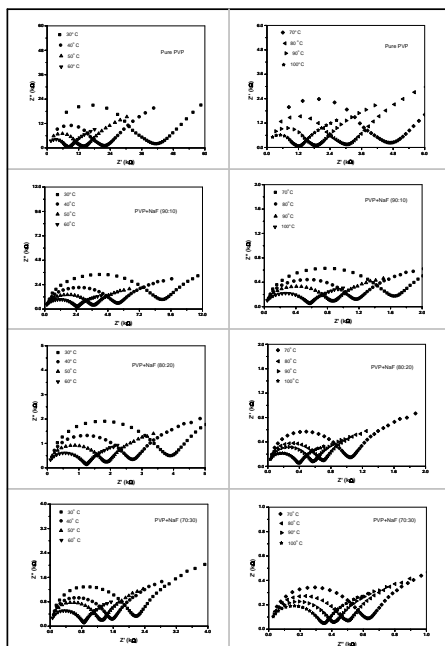


Fig - 3: Impedance (Cole-Cole) plots of Pure PVP and (PVP+NaF) polymer films at different temperatures

The variation of conductivity (σ), as a function of NaF salt concentration in PVP is shown in Fig-4 in the temperature range of 303 – 363 K. From the figure, it is seen that the conductivity of pure PVP is about $3.11 \times 10^{-7} \text{ Scm}^{-1}$ at room temperature and increases to $1.44 \times 10^{-6} \text{ Scm}^{-1}$ for 10 wt% NaF. The increase in conductivity becomes flatter on further addition of NaF upto 30 wt% to the polymer. For 40 wt% of NaF to the polymer the conductivity decreases. This may be due to the increasing influence of the ion pairs, ion triplets and higher ion aggregations, which reduces the overall mobility and degree of freedom [12].

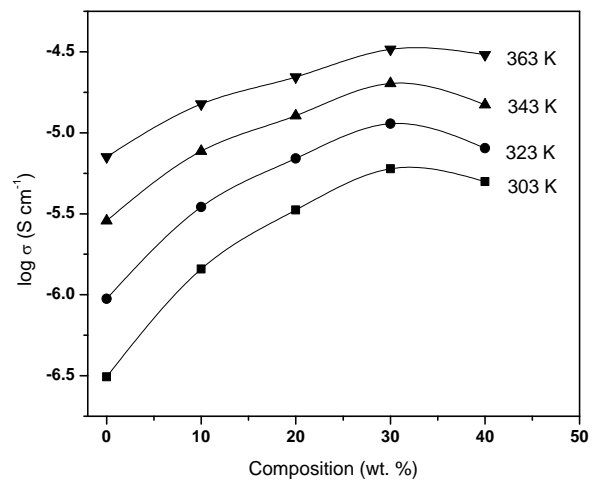


Fig - 4: Composition vs conductivity plots of PVP+NaF polymer electrolyte system at different temperatures

The variation of conductivity as a function of temperature for pure and different concentrations of NaF salt in PVP is shown in Fig-5 over a temperature range 303 – 373 K. In the temperature range of study, the values of ionic conductivity are found to increase with increasing temperature in all compositions include pure film. This may be explained on the basis of an increase in either ionic mobility or the concentration of carrier ions [13]. The observed Arrhenius behavior is in agreement with the theory established by Tareev [14]. This may be rationalized by considering the free volume model [15]. Durger [16] have attributed to the change in the conductivity with temperature in solid polymer electrolytes to segmental (polymer chain) motion, which results in an increase in the free volume of the system. The segmental motion either permits the ions to hop from one site to another or provides a path way for ions to move.

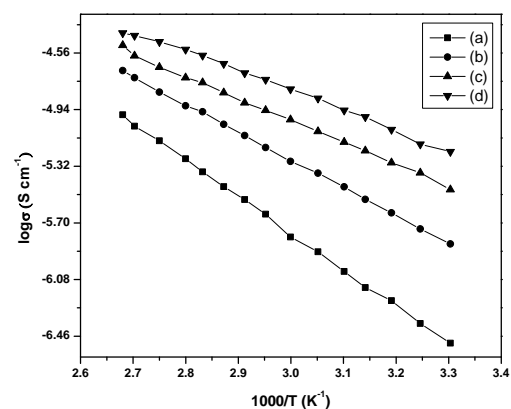


Fig - 5: Temperature-dependant conductivity of (a) pure PVP, (b) PVP+NaF (90:10), (c) PVP+NaF (80:20) and (d) PVP+NaF (70:30)

3.4 Transference number

Electronic and ionic transference number measurements play an important role in explaining the conductivity of the polymer electrolyte system. The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport have been evaluated in the (PVP+NaF) electrolyte system using Wagner's polarization technique [6]. In this technique dc current was monitored as a function of time on application of fixed dc voltage across the Na/polymer electrolyte/C. After polarization of the cell with 1.5 V dc, the current versus time plots were obtained and shown in Fig- 6.

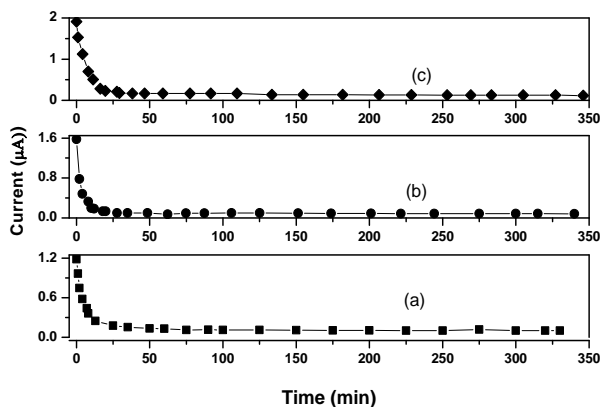


Fig - 6: Current vs time plots of (a) PVP+NaF (90:10) (b) PVP+NaF (80:20) (c) PVP+NaF (70:30) polymer electrolytes

The transference numbers (t_{ion} and t_{ele}) are calculated from the polarization current versus time plots using the equations:

$$t_{ion} = 1 - I_f / I_i \quad (4)$$

$$t_{ele} = 1 - t_{ion} \quad (5)$$

where ' I_i ' is the initial current, and ' I_f ' is the final residual current.

For all the compositions of (PVP+NaF) electrolyte system, the values of ionic transference numbers are in the range 0.91 - 0.93. This suggests that the charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from electrons [17].

3.5 Discharge profiles

Solid state electrochemical cells were fabricated with the configuration Na(anode)/polymer electrolyte/(I₂ + C + electrolyte)(cathode) using (PVP+NaF) polymer electrolyte films. Sodium 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 Na/ (PVP+NaF) (90:10)/(I₂+C+electrolyte), Na/(PVP+NaF)(80:20)/(I₂+C+ electrolyte) and Na/(PVP+NaF)(70:30)/(I₂+C+ electrolyte) cells at ambient temperature for constant load of 100 kΩ are presented in Fig-7. The sharp initial decrease in

voltage may be due to the polarization and/or the formation of thin layer sodium at electrode-electrode interface [18].

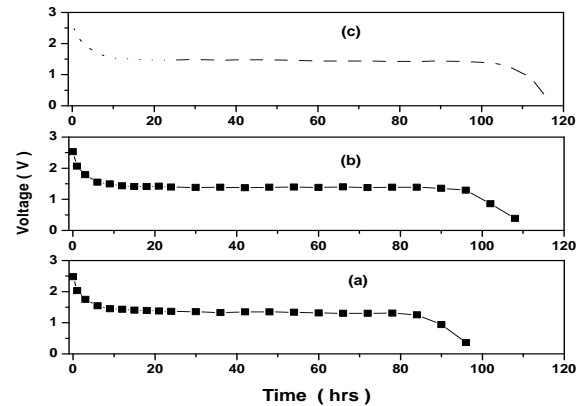


Fig - 7: Discharge characteristics of (a) PVP+NaF (90:10) (b) PVP+NaF (80:20) (c) PVP+NaF (70:30) electrochemical cells

Table: Various cell parameters for (PVP+NaF) polymer electrolyte system

Cell parameters	Na/(PVP+NaF) (90:10)/ I ₂ +C+ electrolyte	Na/(PVP+NaF) (80:20)/ I ₂ +C+ electrolyte	Na/(PVP+NaF) (70:30)/ I ₂ +C+ electrolyte
OCV (V)	2.48	2.53	2.64
SCC (mA)	1.17	1.32	1.39
Cell area (cm ²)	1.33	1.33	1.33
Cellweight (grams)	1.12	1.12	1.12
Time (h)	82	97	106
Discharge capacity (mA/h)	0.0142	0.0136	0.0131
Power density (W/Kg)	2.59	2.98	3.27
Energy density (Wh/Kg)	212	290	347
Current density (mA /cm ²)	0.88	0.99	1.05
Load (kΩ)	100	100	100

The cell parameters were calculated and are shown in the Table. From the data, it is clear that the short circuit current (SCC), open circuit voltage (OCV) and discharge time for the plateau region were found to be greater in (PVP+NaF; 70:30) cell comparable to the other complexed films. This may be due to the high ionic conductivity and higher degree of amorphosity of this system when compared to other systems. The cell parameters of the present electrolyte system are comparable with the earlier work reported on different polymer electrolyte systems [19-21]. This supports the practical application of the present electrolyte in solid-state battery applications.

4. CONCLUSIONS

XRD patterns of the (PVP+NaF) showed the decrease of intensity of peaks corresponding to pure PVP with the increase of salt wt% ratio suggesting a decrease in the crystallinity of the complex. The conductivity was found to increase with increase of dopant concentration and temperature in pure PVP as well as in all compositions of (PVP+NaF) polymer electrolytes. The ionic transport number data in the (PVP+NaF) polymer electrolyte films indicate that the conduction is due to ions rather than electrons. Using these films, electrochemical cells were fabricated and the parameters of the cells are compared with those reported by earlier workers. Thus, (PVP+NaF) electrolytes are found to be worthy candidate for solid-state batteries.

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