

Preparation and characterization of (PVP +NaCl) based polymer electrolytes for electrochemical cell applications

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Abstract: Polymer electrolyte films based on polyvinyl pyrrolidone (PVP) complexed with sodium chloride (NaCl) were prepared by solution casting technique. The complexation of NaCl salt with the polymer was confirmed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopic (FTIR) studies. The conductivity and dielectric measurements were carried out on these films in the frequency range 100Hz to 1MHz and temperature range 303K to 360 K. The complex impedance spectroscopy results reveal that the high-frequency semicircle is due to the bulk effect of the material. The conductivity was found to increase with the increase of salt concentration. The temperature dependence of ionic conductivity of these electrolytes exhibited Arrhenius behavior. The value of activation energy decreases with increasing salt concentration. Transference numbers were carried out using Wagner's polarization technique. The charge transport in this electrolyte system is predominantly due to ions. Electrochemical cells were fabricated with the configuration Na / (PVP+ NaCl) / (I₂+C+electrolyte) and various parameters of the cells including open circuit voltage (OCV), short circuit current (SCC), power density etc., were evaluated. The performance of the electrochemical cells in the present investigations compares favorably with the parameters of earlier workers on different electrolyte systems, which clearly indicates the applicability of the present electrolyte systems as potential candidates for solid state electrochemical cells.

Keywords: Polymer electrolytes, ionic conductivity, electrochemical cells



Introduction

The study of ionic conductivity in polyether-based hosts complexed with alkali metal salts has generated research activities leading to significant advances in the material characteristics of these polymer-salt complexes and also in their structure[1,2]. Lithium-ion conducting polymer electrolytes are of great research interest owing to their possible application to lithium-polymer batteries with high-energy density [3]. Among the various types of polymer electrolyte systems used in lithium polymer batteries, solid polymer electrolytes (SPEs) have many advantages such as high ionic conductivity, high-energy density, leak proof, solvent-free condition, wide electrochemical stability windows, easy process ability and light weight. Till now different polymers, such as PAN , PMMA and PVdF were studied with these advantages in mind[4-6]. A few attempts have tried polymer electrolytes based on potassium ion complexes films [7, 8]. The

main advantage of using potassium metal ion is its availability in abundance at a cheaper cost than lithium. Further, more softness of the material makes it easier to achieve good contact with other components in the battery. In the present investigations, our intension is mainly focused on the preparation and characterization of PVP based polymer electrolytes using potassium chloride as dopant and verifying its potential for the usage of solid state batteries.

Experimental

Films of pure PVP and NaCl salt complexed films were prepared with weight percent ratios (90:10), (80:20) and (70:30) by solution casting technique using triple distilled water as solvent. The solutions were stirred for 10-12 hours to get a homogenous mixture and then casted on to polypropylene dishes and allowed to evaporate slowly at room temperature. The final product was vacuum dried thoroughly. The XRD patterns of the films were recorded with a Seifert-3003 TT X-ray diffractometer. FTIR spectra of these films were recorded using EO-SXB IR spectrometer with a resolution of 4 cm^{-1} . The measurements were taken over a wave number range of $400 - 4000\text{ cm}^{-1}$. AC Impedance measurements were carried out by a computer controlled phase sensitive multimeter (PSM1700) in the frequency range $0.1\text{ kHz} - 1\text{MHz}$ and temperature range $300 - 360\text{ K}$.

Results and Discussion

XRD analysis

X-ray diffraction pattern is essential to obtain the detailed structure, knowledge on the given material. If the material under investigation is crystalline, well defined peaks are observed, while non-crystalline or amorphous systems show a broad instead of well defined peaks. The X-ray diffraction pattern of pure PVP, sodium chloride salt and PVP complexed with NaCl were shown in Fig. 1. In the figure, the pure PVP shows a characteristic peak at 14° indicating its semi crystalline nature. The intensity of this peak gradually decreases with the increase of sodium chloride salt. This could be due to the disruption of the PVP crystalline structure by NaCl. This shows a decrease in the degree of crystallinity of polymer after the addition of salt. No sharp peaks were observed for higher concentrations of NaCl salt in the polymer, suggesting the dominant presence of amorphous phase [7].

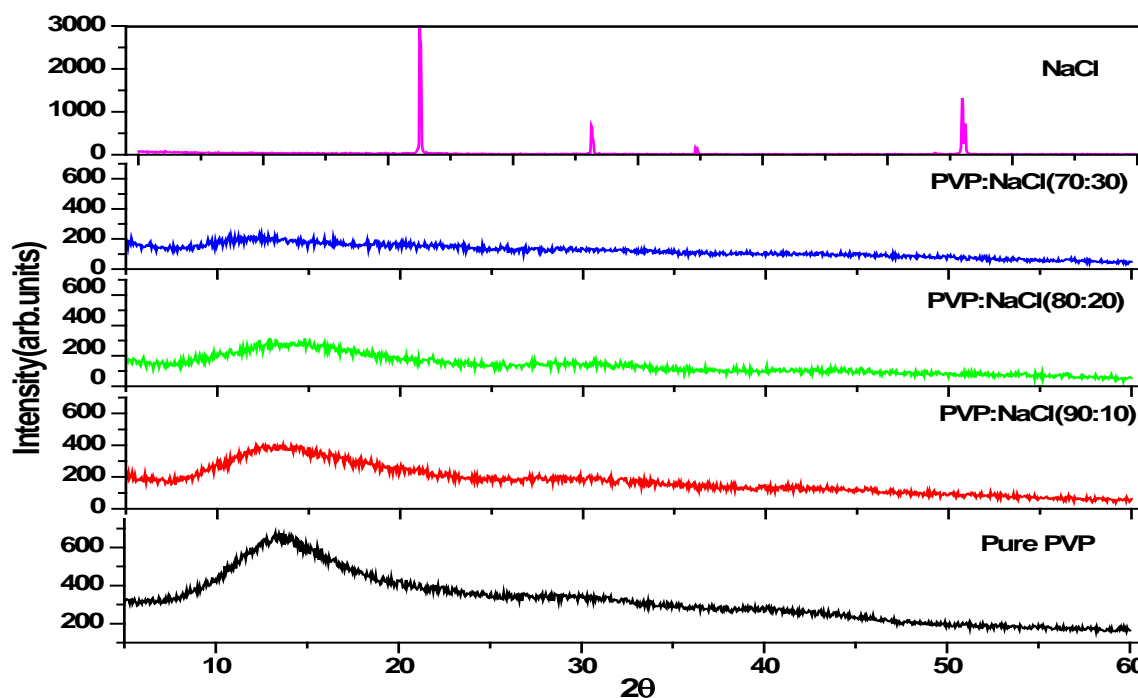


Fig 1: XRD analysis of PVP, NaCl and NaCl doped PVP polymer electrolyte films

FTIR studies

FTIR spectroscopy is an important tool to investigate the information about the complexation and interactions between the various constituents in the polymer electrolyte. Fig.2 shows the FTIR spectra of pure PVP, NaCl complexed PVP and NaCl salt. The absorption band in the region 2874cm^{-1} is due to the intermolecular hydrogen bonded with carbon C-H stretching frequency of pure PVP which is shifted to 2922cm^{-1} , 2939cm^{-1} and 2952cm^{-1} in the 05%, 10%, and 15% salt complexed PVP films respectively. In addition to this, the C-N stretching showed an absorption band at 2151cm^{-1} in pure PVP and is shifted to 2137cm^{-1} , 2131cm^{-1} and 1878cm^{-1} for 05%, 10% and 15% salt complexed PVP films respectively. Similarly for C=O stretching for pure PVP is 1750cm^{-1} and is shifted to 1752cm^{-1} , 1755cm^{-1}

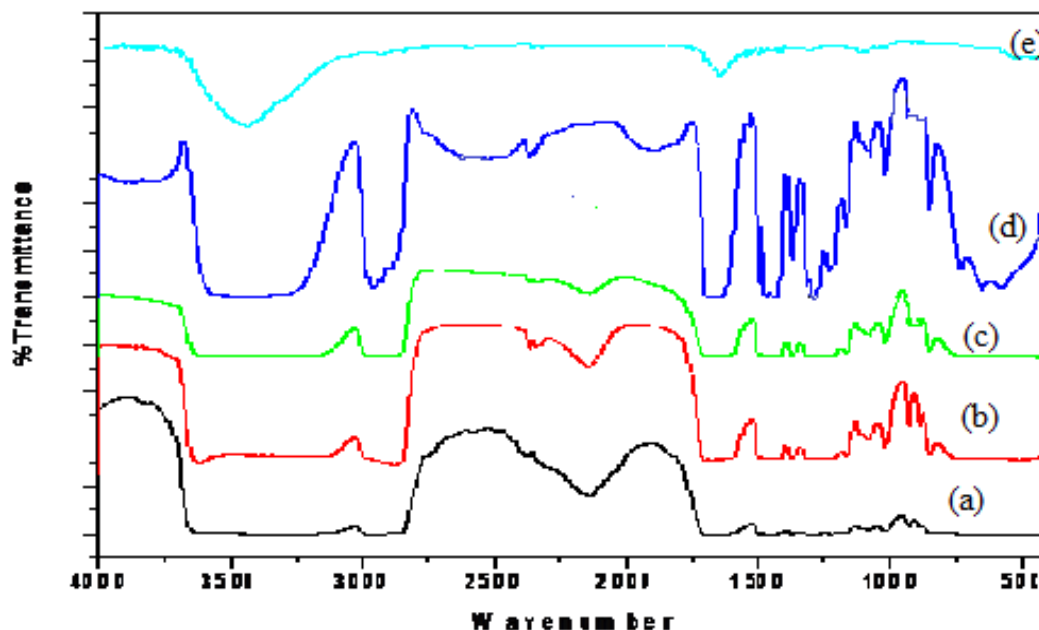


Fig.2 Fourier Infrared Spectra of (a) pure PVP (b) PVP: NaCl (90:10) (c) PVP: NaCl (80:20) PVP (d) PVP: NaCl (70:30) and (e) pure NaCl salt

and 1760 cm^{-1} for 05%, 10% and 15% salt complexed PVP films. The C-C stretching for pure PVP is 1704 cm^{-1} for Pure PVP and is shifted to 1710 cm^{-1} , 1713 cm^{-1} and 1716 cm^{-1} for 05%, 10% and 15% salt complexed PVP films. The C-H bending in pure PVP exhibited absorption at 1465 cm^{-1} is also shifted to 1459 cm^{-1} , 1453 cm^{-1} , and 1439 cm^{-1} for 05%, 10% and 15% salt complexed PVP films. Finally the deformation is coupled to C-H wagging and gives rise to a peak at 1382 cm^{-1} in pure PVP which is shifted to 1374 cm^{-1} , 1370 cm^{-1} and 1368 cm^{-1} in the complexed films due to complexation of salt. All these changes in the FTIR spectra are clear indications for the complexation of PVP with NaCl salt.

Impedance analysis

Fig .3shows the typical real (Z') and imaginary (Z'') parts of the impedance data plotted in complex impedance plane for (PVP+ NaCl) doped polymer electrolyte films at different temperatures. The complex impedance diagram shows two well defined regions, the high frequency region semicircle which is due to the bulk effect of the electrolyte and the linear region in the lower frequency range is attributed to the effect of the blocking electrodes. In an ideal case at low frequency, the complex impedance plots should show the straight line

parallel to the imaginary axis, but the double layer at the blocking electrodes causes the curvature [9]. The conductivity of the polymer electrolyte was calculated from the measured resistance, area and thickness of the polymer film, according to the formula:

$$\sigma = l/R_bA$$

where l is the thickness (cm) of the polymer electrolyte, A the area of the blocking electrode (cm^2), and R_b is the bulk resistance of the polymer.

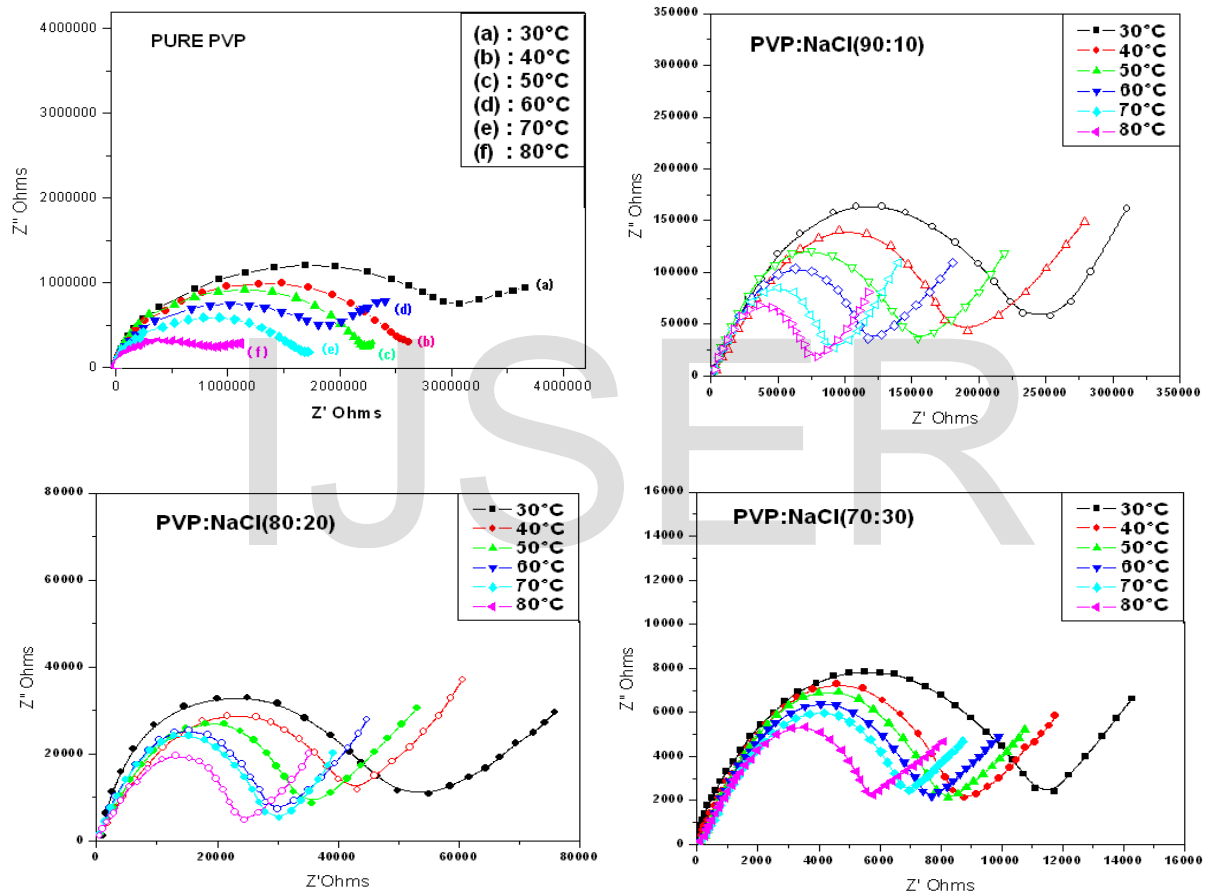


Fig 3: Cole-Cole plots for PVP: NaCl at different temperatures

The bulk electrical resistance (R_b) of the material is obtained from the Cole-Cole plots with the intercept of the high frequency side on the X-axis. The bulk resistance decreases with increasing temperature. The decrease in resistance of the polymer electrolyte is due to the enhancement of the ionic mobility and the number of carrier ions with temperature [10].

Fig .4 shows the variation of $\log(\sigma)$ with inverse absolute temperature for various PVP: NaCl complexes. From the figure, the conductivity was found to increase with the increase of temperature. This can be explained on the basis of the free volume model [11] and hopping of charge carriers between the localized states .Since Poly vinyl pyrrolidone is a linear polymer with carbon chain as the back bone, the polymer chains which are less entangled are capable of causing electrical conductivity. Further PVP being a polar polymer, ionizes the NaCl salt into anions and cations under the influence of the applied electric field and temperature. These ions hop between the localized states and cause the enhanced conductivity. Further, when temperature increases, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur .Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence the conductivity. Hence, the increment of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobility. The amorphous nature also provides a bigger free volume in the polymer electrolyte system upon increasing temperature. [12].

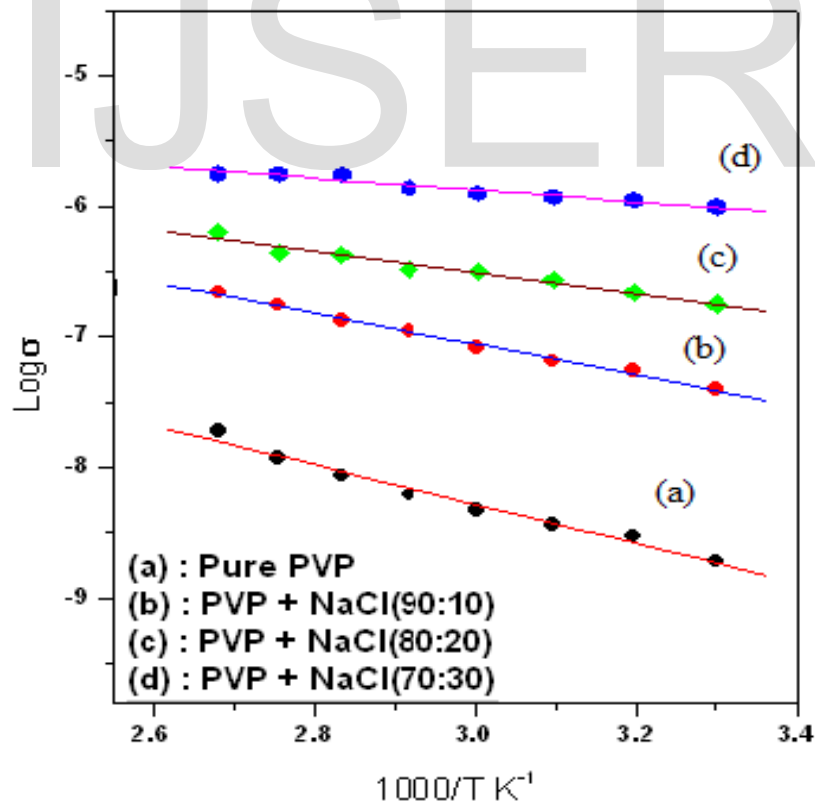


Fig 4: Variation of $\log \sigma$ vs. $1000 / T$ for pure PVP and NaCl doped films

The activation energies were calculated from $\log \sigma$ vs. $1000/T$ plots using the following Arrhenius equation.

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

where σ_0 is a constant, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. These values are tabulated in table 1. The low activation energy for sodium ion transport is due to dominant presence of amorphous nature of polymer electrolyte that facilitates the fast Na^+ ion motion in polymer network.

Transference numbers

In order to verify the dominant conducting species in the present electrolyte system, Transference number measurements were carried out using well known Wagner's polarization technique [13]. In this method, the dc current was monitored as a function of time on application of a fixed dc voltage of 1.5 V across the cell $\text{Na}/(\text{PVP} + \text{NaCl})/\text{C}$. The current vs. time plot of (PVP + NaCl) is shown in Fig. 5. From the figure, the transference numbers (t_{ion} and t_{ele}) have been evaluated using the formula

$$t_{\text{ion}} = 1 - I_f/I_i \quad \text{and} \quad t_{\text{ele}} = 1 - t_{\text{ion}}$$

where I_i and I_f are the initial and final currents, respectively. The resulting data are shown in table 2 for all the compositions of the (PVP: NaCl) electrolyte system, the values of the ionic transference number are close to unity. This suggests that the charge transport in these polymer electrolyte films is predominantly to ions rather than electrons.

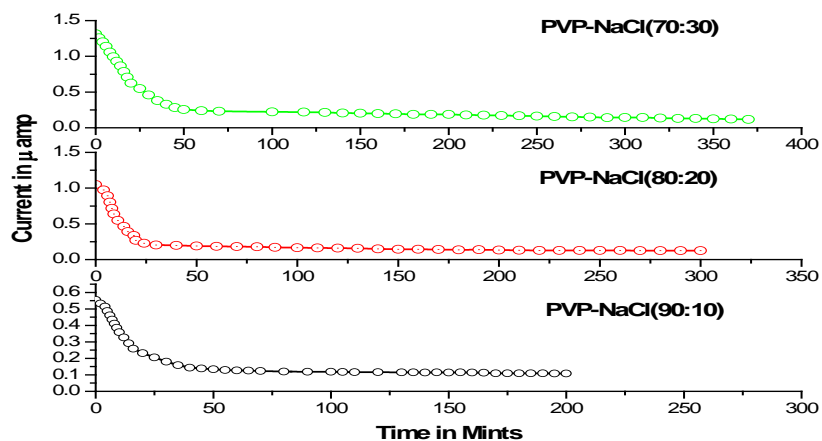


Fig 5: Transference number measurements for PVP: NaCl doped polymer electrolyte films

Battery discharge characteristics

The discharge characteristics of the cell Na/ (PVP + NaCl) / (I₂ + C + electrolyte) at an ambient temperature for a constant load 100 k Ω is shown in Fig.6. 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 potassium at the electrode - electrolyte interface. The cell parameters like open circuit voltage (OCV), short circuit current (SCC), current density etc., were evaluated for all the batteries and are given in table 3. From the table it is clear that, cell with the composition (PVA: NaCl) (85:15) exhibits better performance and stability than the other compositions. These results are in well comparison with the existing reports and are even better [14].

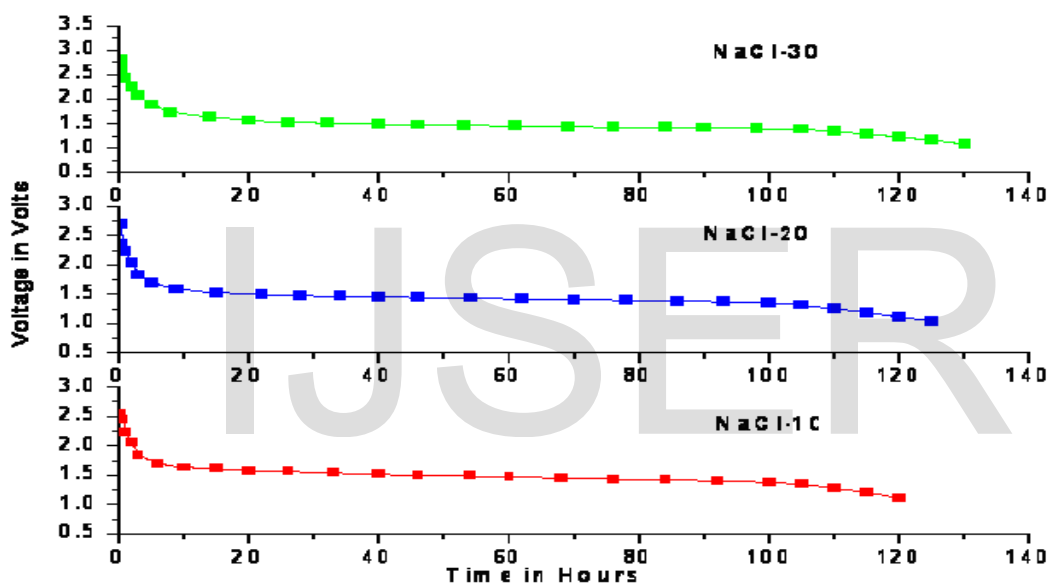


Fig: 6 Discharge characteristics of PVP: NaCl doped polymer electrolyte films

Conclusions

PVP based electrolyte films were prepared using solution casting technique. The XRD pattern reveals the increase in amorphous nature of the film with the addition of salt. The electrical conductivity was found to increase with the increase of temperature. From transference measurements it is clear that, the conduction mechanism in these electrolyte systems is predominantly due to ions rather than electrons. Using (PVP: NaCl) polymer electrolyte systems, solid state batteries were fabricated and their discharge characteristics were studied. Among these cells, the cell made up of (PVP: NaCl) (85:15) electrolyte was found to be more stable than the other two cells.

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Tables

Table: 1 Activation energies of NaCl doped PVP polymer electrolyte films

Polymer electrolyte	Composition	Activation energy (eV)
PVP	----	0.452
PVP+NaCl	(95:05)	0.422
PVP+NaCl	(90:10)	0.401
PVP+NaCl	(85:15)	0385

Table: 2 Transference numbers of NaCl doped PVP polymer electrolyte films

Polymer electrolyte	Composition	Transference numbers	
		t_{ion}	t_{ele}
PVP	--		
PVP+NaCl	(95:05)	0.94	0.06
PVP+NaCl	(90:10)	0.95	0.05
PVP+NaCl	(85:15)	0.96	0.04

Table: 3 Cell parameters of NaCl doped PVP polymer electrolyte films

Cell parameters		(PVP+NaCl) (95:05)	(PVP+NaCl) (90:10)	(PVP+NaCl) (85:15)
Open circuit voltage	(V)	2.543	2.686	2.793
Short circuit current	(μA)	782	897	998
Area of the cell	(cm^2)	1.32	1.32	1.32
Weight of the cell	(g)	1.12	1.13	1.15
Discharge time for plateau region	(hours)	101	105	110
Current density	($\mu A cm^{-2}$)	592.4	679.5	756.05
Power density	($W kg^{-1}$)	1.775	2.132	2.423
Energy density	($W h kg^{-1}$)	179.27	223.86	266.53
Discharge capacity	($\mu A h^{-1}$)	7.742	8.542	9.072