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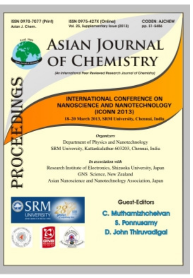

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Structural and A.C. Conductivity Studies of (PVdF + $NaClO_4$) Solid Polymer Electrolyte System for an Electrochemical Cell Applications†

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An investigation is carried out on a new solid polymer electrolyte system consisting of poly(vinylidene fluoride) (PVdF) as a host polymer, sodium perchlorate, as salt. Solid polymer electrolyte films were prepared by solution-casting technique and characterized by using IR, DSC, composition-dependence conductivity and transference number studies. IR studies revealed that the complexation of the polymer poly(vinylidene fluoride) with $NaClO_4$. Differential scanning calorimetery was used to determine the melting temperatures of the pure and complexed films. The maximum ionic conductivity for 60 PVdF + 40 $NaClO_4$ polymer electrolyte system was found to be 1.78×10^{-5} S/cm at room temperature. Transference number data suggests that the charge transport in this polymer electrolyte system is mainly due to ions. Electrochemical cells were fabricated with the configuration of $Na^+/(PVdF+NaClO_4)/(I_2+C+electrolyte)$ and discharge characteristics were studied under a constant load of 100 KΩ. Various cell parameters, such as open circuit voltage, short circuit current, power density and energy density were determined.

Key Words: Polymer electrolyte, Ionic conductivity, IR, Transference number, Electrochemical cell.

INTRODUCTION

The polymeric electrolytes have a unique hybrid structure, which possesses cohesive properties of solids and diffusive properties of liquids simultaneously. The solvent or salt-solution is retained in solid polymeric electrolyte and helps in ionic conduction process, whereas the host polymer matrix provides applications as electrolytes/separators in rechargeable batteries, super capacitors, fuel cells and other electrochemical devices[1-4]. Many research groups have reported various polymer electrolytes based on lithium, magnesium and zinc salts to realize respective battery systems. Particularly, the Li based batteries, which are mostly reported in literature, suffer from some safety limitations and many other problems[5,6]. So, their alternatives in the form of magnesium, zinc and sodium batteries are reported, although these are not extensively studied[7-9]. The development of sodium rechargeable batteries would be an interesting study as sodium may be considered as an alternative to lithium as a negative electrode (anode) due to its low cost, natural abundance, non-toxicity, low atomic mass (23.0) and high electrochemical reduction potential[10-12]. It is therefore a need to develop high sodium ion conducting non-aqueous electrolytes suitable for the fabrication of rechargeable sodium batteries. The development of sodium ion conducting polymer electrolytes should be preferred in view of their higher conductivity values (comparable to liquid electrolytes), mechanical and electrochemical properties.

In consistence with the rapid progress in size, thickness reduction of electronic devices and development of multimedia industries in recent years, demand has been increasing to fabricate small sized portable devices. Today it is almost universally accepted that such combination of size and thickness can only be obtained by using non conventional electrodes and electrolyte materials and that the most promising choices are those based on lithium operating systems. With this situation, attempts have been made in poly(ethylene oxide) (PEO) based polymer electrolytes to reach an appreciable electrical conductivity at ambient temperature[13-15]. Generally solid polymer electrolytes have many advantages, *viz.* high ionic conductivity, high specific energy, wide electrochemical stability windows, light and easy possibility. The conductivity is related to the glass transition temperature, T_g and is further related to the inter-linking of the polymer chain. The polymer poly(vinylidene fluoride) (PVdF) is of semi crystalline nature and the electrolytes based on PVdF are expected to have high anodic stabilities due to strong electron withdrawing functional groups and also they have high permittivity, relatively low dissipation factor and high dielectric constant.

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In the present investigation, structural, thermal and AC conductivity studies have been performed on poly (vinylidene fluoride) (PVdF) based polymer electrolytes with $NaClO_4$ as salt. The authors report solid ion conducting polymer electrolyte based on (PVdF) system. Several analytical techniques, such as IR and DSC studies, composition dependent conductivity and transport number measurements were performed to characterize these polymer electrolytes. Based on these electrolytes, an electrochemical cell was fabricated with the configuration anode/polymer electrolyte/cathode.

The discharge characteristics of the cell have been studied at a constant load of 100 KΩ. The results of these investigations are reported in this present paper.

EXPERIMENTAL

Pure PVdF (Aldrich, M.W ≈ 5.4×10^5) complexed with a fine powder of sodium perchlorate were prepared in the stoichiometric ratios (80:20), (70:30) and (60:40) by a solution-cast technique using dimithyl formide (DMF) as solvent. PVdF was used as the polymer. $NaClO_4$ was added accordingly. The mixture of these solutions was stirred for 12 h to obtain a homogeneous solution. The solution was then poured into the polypropylene dishes and evaporated slowly at room temperature under vacuum. The polymer electrolyte films were then transferred into a desiccator for further drying before the test.

The IR spectra in these films were recorded with the help of JASCO FT/IR-5300 spectrophotometer in the range 400-4000 cm^{-1}. The differential scanning calorimetry pattern of pure PVdF and PVdF complexed with $NaClO_4$ for the (80:20), (70:30) and (60:40) compositions were studied using DSC (model TA 2010). The AC conductivity has been measured using the HP Complex Impedance spectra with computer controlled set up in the temperature range 298-373 K. The ionic and electronic transport numbers (tion and tele) were evaluated by means of Wagner's dc polarization technique[16]. In this technique, a freshly prepared film of (PVdF+ $NaClO_4$) under a DC bias (step potential 1.5V) was used. The resulting current was monitored as a function of time with a Keithly electrometer (Keithly Inc., USA, Model 614).

An electrochemical cell was fabricated with the configuration Na+/(PVdF + $NaClO_4$)/(I_2 + C + electrolyte). The discharge characteristic studies of these electrochemical cells were monitored at a constant load of 100 KΩ.

RESULTS AND DISCUSSION

The IR spectra of pure PVdF, PVdF complexed with $NaClO_4$ and pure $NaClO_4$ were recorded with the help of JASCO IR-5300 spectrophotometer in the range 4000-400 cm^{-1} (Fig. 1). The complexation of pure PVdF with $NaClO_4$ salt is extensively studied using IR spectroscopy. The intensity of the aliphatic CH_2 stretching vibrations band observed around 2890 cm^{-1} in PVdF was found to decrease with the increase in the concentration of $NaClO_4$ salt in the polymer. The width of the C-F stretching band observed at around 1693 cm^{-1} in PVdF also showed an increase in the salt concentration in the polymer. Also the appearance of new peaks along with changes in existing peaks (and/or their disappearance) in the IR-spectra directly indicates the complexation of PVdF with $NaClO_4$. This IR data clearly establishes the complexation of $NaClO_4$ with different weight ratios of the polymer PVdF.

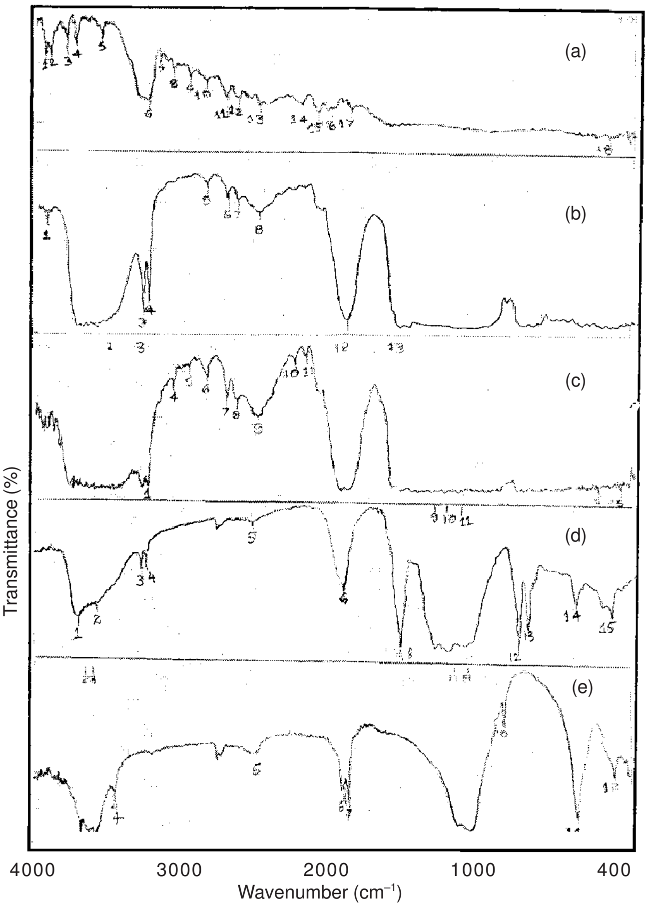

Fig. 1. IR spectra of a) Pure PVdF, b) PVdF + $NaClO_4$ (80:20), c) PVdF + $NaClO_4$ (70:30), d) PVdF + $NaClO_4$ (60:40) and e) pure $NaClO_4$ salt

The differential scanning calorimetry curves of pure PVdF and PVdF complexed with $NaClO_4$ of 80:20, 70:30 and 60:40 compositions are shown in Fig. 2. An exothermic peak was observed at 150.4 °C, which corresponding to melting temperature (T_m) of pure PVdF. The slight shift in the melting point (T_m) towards higher temperature has been observed due to the addition of $NaClO_4$ salt to the polymer. Earlier workers[17-19] have also reported similar result on polymer complexed system. The melting temperature values of these polymer electrolyte films are given in Table-1.

TABLE-1
MELTING TEMPERATURE VALUES OF PVdF AND VARIOUS POLYMER ELECTROLYTE SYSTEMS OBTAINED FROM DSC STUDIES

System	Melting temperature (T_m) in °C
Pure PVdF	150.7
PVdF + $NaClO_4$ (80:20)	151.2
PVdF + $NaClO_4$ (70:30)	154.8
PVdF + $NaClO_4$ (60:40)	152.9

Impedance spectroscopy is a relatively new and powerful method for characterizing many of the electrical properties of

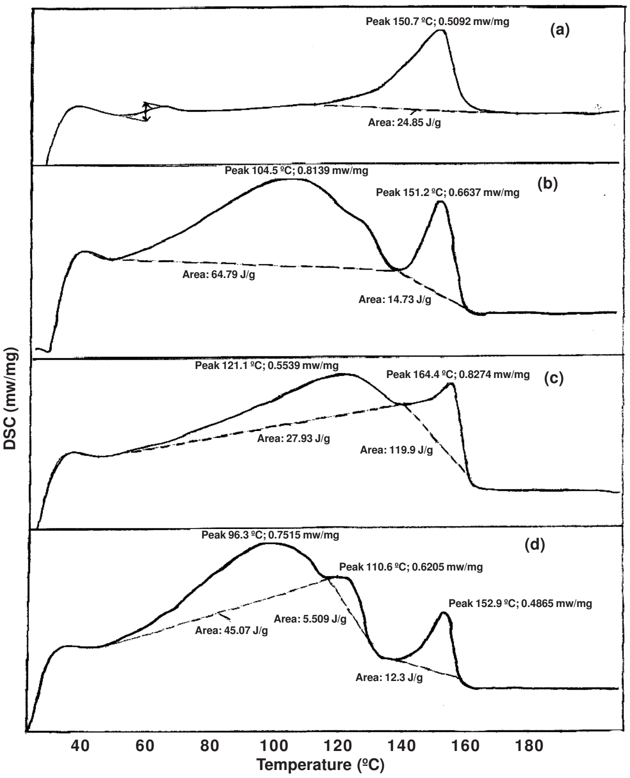

Fig. 2. DSC curves of a) Pure PVdF, b) PVdF + $NaClO_4$ (80:20), c) PVdF + $NaClO_4$ (70:30) and d) PVdF + $NaClO_4$ (60:40)

electrolyte materials and their interfaces with electronically conducting electrodes. An Impedance plot (plot between the real and the imaginary parts of impedance) for PVdF: $NaClO_4$ polymer complexes with different weight percent ratios are shown in Fig. 3. The plots consist of a high-frequency broadened semicircle due to a frequency-dependent capacitor (C_g) parallel to the bulk resistor. The point where the semicircle intersects the real axis gives the value of the bulk resistance (R_b). By knowing the bulk resistance (R_b) along with the dimensions of the sample, one can calculate the conductivity of the sample by using the relation.

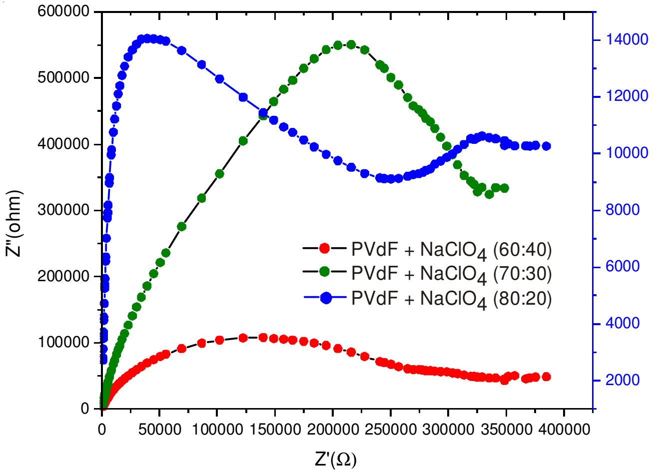

Fig. 3. Complex impedance plot for the [PVdF:$NaClO_4$] polymer electrolyte system at room temperature (298K). Z *vs.* Z plots of complex impedance spectra PVdF + $NaClO_4$ (60:40) O PVdF + $NaClO_4$ (70:30) O PVdF + $NaClO_4$ (80:20)

$$\sigma = t/R_bA \tag{1}$$

where t and A are the thickness and the area of the polymer electrolyte samples, respectively.

The variation of AC conductivity (σ) as a function of $NaClO_4$ composition in PVdF at room temperature (298 K) and 373 K is given in Fig. 4.

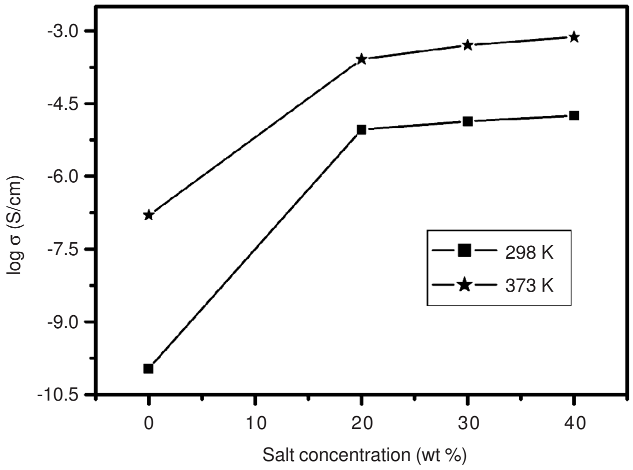

Fig. 4. Effect of the concentration of NaClO4 on the conductivity of PVdF at different temperatures (398 K and 373 K)

The following conclusions can be drawn.

- The conductivity of pure PVdF is approximately 10^{-10} S/cm at room temperature and its value increases sharply to 10^{-6} S/cm on complexing with 20 wt % $NaClO_4$. The increase in conductivity becomes slower on further addition of $NaClO_4$ to the polymer. The maximum conductivity was found to be 7.46×10^{-4} S/cm at 373 K for the 60 PVdF : 40 $NaClO_4$ polymer electrolyte. This behaviour has been explained by various researchers, who have studied PEO based polymer electrolyte in terms of ion association and the formation of charge multipliers[20-22].
- The ionic conductivity in the polymer complexes may be interpreted on the basis of a hoping mechanism between coordinating sites, local structural relaxations and segmented motions of the polymer chains. These are essential to assure high conductivity of the electrolyte. The ionic conductivity values of these polymer electrolyte films at different temperatures are given in Table-2.

Total ionic transference number of polymer electrolyte has been measured by Wagner's DC polarization technique[16], which is used to determine the ionic contribution to the total charge transport by measuring the residual electronic current passing through the electrolytes. Three Wagner polarization cells Na+/Polymer electrolyte/(I_2+C+electrolyte) were prepared by coating silver paste as blocking electrode on to the faces of PVdF+$NaClO_4$ based composition polymer electrolyte systems. A fixed small dc potential (1.5 V) has been applied across the blocking electrodes and the current passing through the cells is measured as a function of time for one hour to allow the samples to become fully polarized are shown in Fig. 5.

Initial total current (I_T) which is the sum of ionic (I_i) and electronic (I_e) currents ($I_T = I_i + I_e$) and final current after polarization which is only the electronic current (I_e) are

TABLE-2
IONIC CONDUCTIVITY AND TRANSFERENCE NUMBER VALUES OF PVdF + $NaClO_4$ SOLID POLYMER ELECTROLYTES AT DIFFERENT TEMPERATURES

Sample PVDF: $NaClO_4$	Conductivity (S/cm)				Transference number	
	298 K	328 K	358 K	373 K	t_{ion}	t_{ele}
PVDF	1.09×10^{-10}	1.06×10^{-10}	2.16×10^{-10}	1.58×10^{-7}	-	-
(80:20)	9.25×10^{-6}	1.11×10^{-5}	1.35×10^{-5}	2.60×10^{-4}	0.91	0.09
(70:30)	1.36×10^{-5}	1.55×10^{-5}	1.77×10^{-5}	5.07×10^{-4}	0.92	0.08
(60:40)	1.78×10^{-5}	1.99×10^{-5}	2.22×10^{-5}	7.46×10^{-4}	0.93	0.07

TABLE-3
CELL PARAMETERS OF [PVdF+$NaClO_4$] SOLID POLYMER ELECTROLYTE CELL SYSTEM FOR A CONSTANT LOAD OF 100 kΩ

Cell parameters	PVdF + $NaClO_4$ (80:20)	PVdF + $NaClO_4$ (70:30)	PVdF + $NaClO_4$ (60:40)
Open circuit voltage (V)	2.52	2.54	2.59
Short circuit current (mA)	0.95	1.30	1.32
Area (cm^2)	1.33	1.33	1.33
Weight (gm)	1.49	138	1.45
Discharge time (h)	65	58	61
Current density (mA/Cm^2)	0.714	0.977	0.992
Power density (watt/kg)	1.61	2.39	2.35
Energy density (watt-hr/kg)	104.4	138.78	143.82

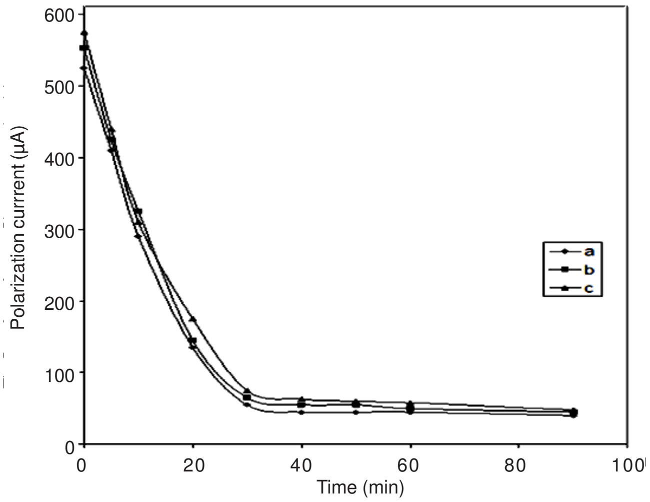

Fig. 5. Polarization current *vs.* time plot of (PVdF + $NaClO_4$) electrolyte system; a) 80:20, b) 70:30 and c) 60:40

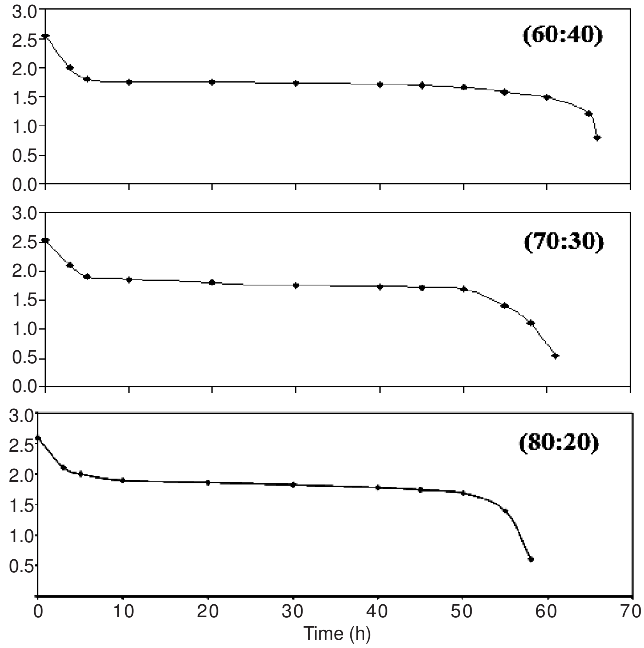

Fig. 6. Discharge characteristics of Na/(PVdF + $NaClO_4$)/(I2 + C + electrolyte) electrochemical cell for a constant load of 100 KΩ

measured. The ionic transference number (t_{ion}) is calculated using the relation

$$t_{ion} = I_i/I_T = (I_T-I_e)/I_T \tag{2}$$

The ionic transference number for all the compositions of the (PVdF + $NaClO_4$) electrolyte system were shown in Table-2. The values of the ionic transference numbers (t_I) are in the range 0.91-0.93 suggest that the charge transport in these polymer electrolyte systems is predominantly ionic accompanied by mass transport and electronic contribution to the total current is negligible.

The area and thickness of the electrolyte are respectively 1.33 cm² and 100 mm. The discharge characteristics are studied for all the cells at room temperature with a constant load of 100 KΩ and are shown in Fig. 6. The initial sharp decrease in the voltage may be due to the polarization effects/or the formation of a thin layer of sodium salt at the electrode-electrolyte interface. The open circuit voltage and short circuit current for these cells are found to be 2.72V and 0.98 mA respectively. The other cell parameters for these cells are evaluated and summarized in Table-3.

On the basis of present study, an electrochemical cell with (PVdF + $NaClO_4$) as electrolyte with improved efficiency is promising. Further work aimed at obtaining higher cell capacities and specific energy is in progress.

Conclusion

The PVdF + $NaClO_4$ solid polymer electrolyte films are prepared successfully. IR spectroscopy confirms the formation of the polymer-salt complex. A change in melting temperature was observed on doping with $NaClO_4$ in PVdF. The conductivity of (PVdF + $NaClO_4$) (60:40) at room temperature was determined to be 1.78×10^{-5} S/cm and at 373 K was 7.46 $\times 10^{-4}$ S/cm. The ionic transport number data in the PVdF + $NaClO_4$ solid polymeric electrolyte films indicate that the conduction is predominantly due to ions. The cell parameters evaluated for the present cell suggest that the present electrolyte system is a worthy candidate for solid state battery application.

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