



Structural and Electrical properties of PVDF based Ag⁺ ion conducting Polymer Electrolyte for Battery Applications

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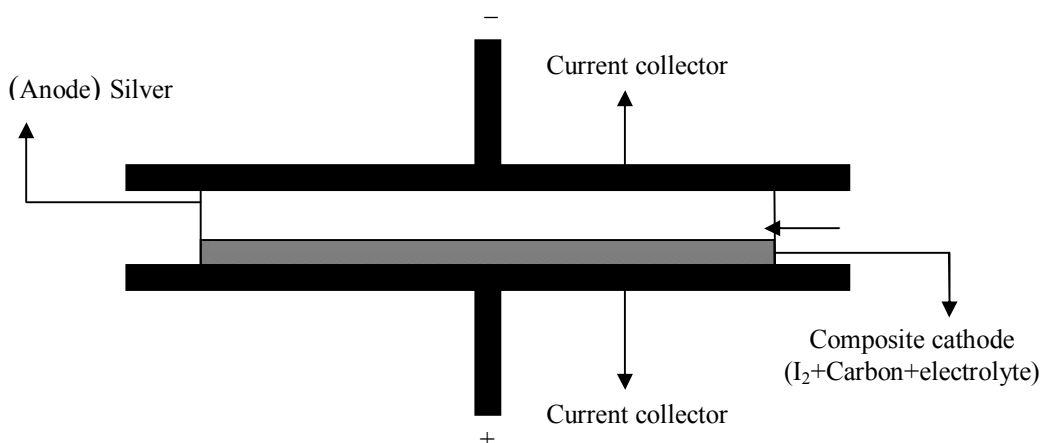
Abstract: An attempt has done on a new solid polymer electrolyte system by blending of poly (vinylidene fluoride) (PVdF), and Silver perchlorate (AgClO₄). Solid Polymer electrolyte films were prepared by solution-casting technique and various characterization techniques has done by using IR, DSC, composition-dependence conductivity and transference number studies. The complexation between the polymers PVdF with salt AgClO₄ was revealed by IR studies. Differential Scanning Calorimetry was used to determine the melting point, glass transition temperatures of solid polymer electrolyte. The high ionic conductivity for PVdF+AgClO₄ (60:40) polymer electrolyte system was found to be 4.20×10^{-5} S/cm at room temperature. The majority charge carrier's takes place in this polymer electrolyte system is mainly due to ions. An Electrochemical cell has been fabricated with the configuration of Ag⁺/(PVdF+AgClO₄)/(I₂+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 calculated.

Keywords: Sol-casting, IR, DSC, A.C Conductivity, Transport properties, Electrochemical Cell.

Introduction

Polymeric electrolytes have unique hybrid structure, which possesses cohesive properties of solids and diffusive properties of liquids simultaneously. Here the solvent or salt-solution is retained in the solid polymer electrolyte and it helps in ionic conductivity process (1). The host polymer matrix provides applications such as electrolytes or separators in fuel cells, super capacitors, rechargeable batteries and other electrochemical storage devices (2,3). Many researchers have reported various polymer electrolytes using sodium, lithium, magnesium, sodium etc. as salts in battery systems. Particularly in the case of Li based batteries, which are mostly reported in literature, have some safety limitations and many problems (4,5). So, their alternatives magnesium and zinc batteries are reported, although these are not extensively studied (Polu and Kumar 2012; Turkovic *et al* 2008; Siva Kumar *et al* 2006)(6,7). Sodium rechargeable batteries were developed and considered them as an alternative to lithium, since sodium acts as anode due to its low cost, natural abundance, non-toxicity, low atomic mass (23.0) and high electrochemical reduction potential (8). So there is a need to develop high sodium ion conducting non-aqueous electrolytes which are suitable for the fabrication of rechargeable sodium batteries. The development of sodium ion conducting polymer electrolytes should be preferred as they have higher conductivity values when compared to liquid electrolytes, mechanical and electrochemical properties (9,10).

Now-a- days there is a 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 (11). 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 (Sreekanth *et al* 2001)(12). 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 (13). Polymer PVdF is of semi crystalline material 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.



Schematic structure of a silver polymer electrolyte rechargeable cell

In the present investigation, structural, thermal and AC Conductivity studies have been performed on poly (vinylidene fluoride) (PVdF) based polymer electrolytes with AgClO_4 as salt. The authors report solid ion conducting polymer electrolyte system based on (PVdF). Techniques, such as IR, 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.

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

Experimental

A new Solid polymer electrolyte films has prepared, Dimethyl formamide (DMF) is used as a common solvent by blending of poly (vinylidene fluoride) (PVdF) (Aldrich, M.W $\approx 5.4 \times 10^5$), and Silver perchlorate (AgClO_4) in the stoichiometric ratios (80:20), (70:30) and (60:40) by a solution - cast technique. PVdF. The mixture of these solutions was stirred for 24 hours to obtain a homogeneous solution. The solution was placed in the polypropylene dishes and evaporated slowly at room temperature under vacuum to remove the solvent traces. The polymer electrolyte films were peeled off then transferred into a desiccator for further drying before the test.

The IR spectra have taken for these films with the help of JASCO FT/IR-5300 spectrophotometer in the range 400-4000 cm^{-1} . X-ray diffraction analysis were carried out by using PHILIPS PW-3710 X-ray diffractometer in the range $2\theta = 10^0 - 70^0$.

The Differential Scanning Calorimetry (DSC) pattern for various compositions was studied using DSC (model TA 2010). The AC Conductivity has been measured using the HP Complex Impedance spectra with the temperature range 298-373K. The ionic and electronic transport numbers (t_{ion} and t_{ele}) were evaluated by means of Wagner's dc polarization technique (Wagner & Wagner 1957). The Transport number and discharge characteristics were calculated with the help of Keithly electrometer (Keithly Inc., USA, Model 614).

An Electrochemical cell was fabricated with the combination of $Ag^+/(PVdF + AgClO_4)/(I_2 + C + \text{electrolyte})$. The discharge characteristic studies of these electrochemical cells were monitored under a dc bias (step potential 1.5V) at a constant load of 100 K Ω .

Results and discussion

IR studies:

The IR spectra is a promising instrument which is used for complexation studies and it is recorded with the help of JASCO IR-5300 spectrophotometer in the range 400-4000 cm^{-1} and are shown in Fig 1.

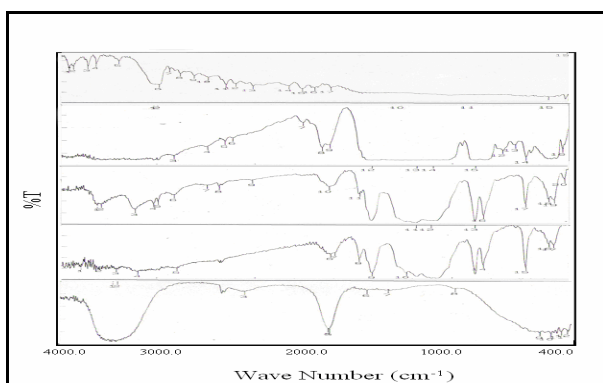


Fig. 1 IR Spectra a) Pure PVdF b) PVdF + $AgClO_4$ (80:20) c) PVdF + $AgClO_4$ (70:30) d) PVdF + $AgClO_4$ (60:40) e) $AgClO_4$ Salt

The complexation formation of PVdF with $AgClO_4$ salt is studied using IR spectroscopy. The schematic of CH_2 stretching vibrations are observed around $2890cm^{-1}$ in PVdF, with the increase in the concentration of $AgClO_4$ salt the stretching band was found to decrease and it is observed in Fig 1. The PVDF exhibits the absorption of a primary alcohol. Hence this absorption takes place the stretching, bending and rocking of C-F stretch, C-C bending, C-O stretch. The width of the C-F stretching band observed at around $1693cm^{-1}$ 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 in the IR-spectra directly indicates the complexation of PVdF with $AgClO_4$.

DSC Studies:

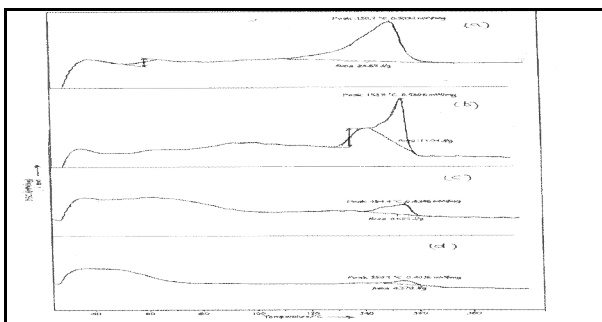


Fig. 2. DSC Spectra a) Pure PVdF b) PVdF + $AgClO_4$ (80:20) c) PVdF + $AgClO_4$ (70:30) d) PVdF + $AgClO_4$ (60:40)

The Differential Scanning Calorimetry (DSC) curves of pure PVdF and PVdF complexed with AgClO_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 AgClO_4 salt to the polymer this results that at the melting point the crystalline nature of the salt and the polymer converts amorphous such that the conductivity nature in polymer film is increasing at the melting point (13). Earlier workers 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 $^\circ\text{C}$
PVdF	150.7°C
PVdF + AgClO_4 (80:20)	153.8°C
PVdF + AgClO_4 (70:30)	154.4°C
PVdF + AgClO_4 (60:40)	154.1°C

Impedance spectroscopy is a promising instrument to measure the electrical and dielectric properties of electrolyte materials. An Impedance plot (plot between the real and the imaginary parts of impedance) for PVdF: AgClO_4 polymer complexes with different weight percent ratios are shown in Fig 3.

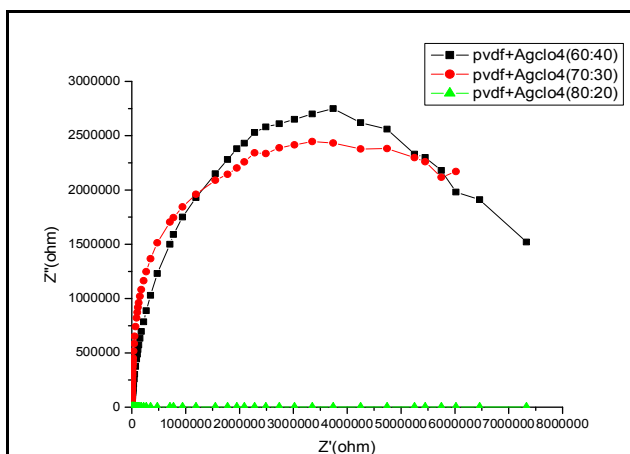


Fig. 3. Complex impedance plot for the [PVdF: AgClO_4] polymer electrolyte system at room temperature (298K). Z'' v s Z' plots of complex impedance spectra ■ PVdF + AgClO_4 (70:30) ■ PVdF+ AgClO_4 (80:20) ■ PVdF+ AgClO_4 (60:40)

The plots consist of a 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

$$\sigma = t/R_b A \quad (1)$$

Where t is the thickness of sample and A is the area of the polymer electrolyte, respectively.

Wt% composition studies:

The variation in logarithmic conductivity sigma as a function for different ratios of AgClO_4 in PVdF. From the graph it is observed that as increasing the salt concentration the conductivity value also increases at a certain level. And it is increasing the order of 10^{-10} to 10^{-4} . Conductivity (σ) as a function of AgClO_4 composition in PVdF at room temperature (298K) and 373K. shown in fig 4

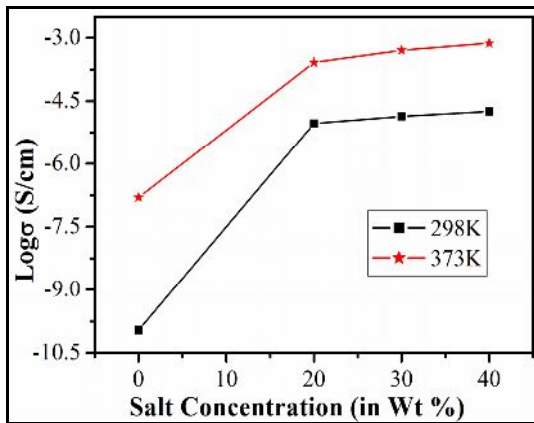


Fig. 4. Effect of the concentration of AgClO_4 on the conductivity of PVdF at different temperatures (398K and 373K).

The following conclusions can be drawn.

1. The conductivity of pure PVdF is 10^{-10} S/cm at room temperature and its value increases sharply to 10^{-7} S/cm at higher temperature. By adding the different weighing ratios to the polymer the ionic conductivity was increased the order of 10^4 the increase in conductivity becomes slower on further addition of AgClO_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 AgClO_4 polymer electrolyte. This behavior has been explained by various researchers, who have studied PEO based polymer electrolyte in terms of ion association and the formation of charge multipliers (14,15).
2. The ionic conductivity in the polymer complexes may be interpreted on the basis of a hopping mechanism between coordinating sites, local structural relaxations and segmented motions of the polymer chains. These are essential to assure high conductivity of the electrolyte (16). The ionic conductivity values of these polymer electrolyte films at different temperatures are given Table 2.

Table 2. Ionic conductivity and Transference number values of PVdF+ AgClO_4 Solid Polymer Electrolytes at different temperatures

Polymer electrolyte system	Conductivity (S.cm^{-1})			
	298 K	328 K	358 K	373 K
PVdF	1.09×10^{-10}	1.06×10^{-10}	2.16×10^{-10}	1.58×10^{-7}
PVdF+ AgClO_4 (80:20)	2.11×10^{-6}	1.31×10^{-5}	1.44×10^{-5}	1.90×10^{-4}
PVdF+ AgClO_4 (70:30)	3.37×10^{-5}	3.55×10^{-5}	3.67×10^{-5}	4.07×10^{-4}
PVdF+ AgClO_4 (60:40)	4.20×10^{-5}	4.36×10^{-5}	4.99×10^{-5}	7.46×10^{-4}

Transport properties:

Total ionic and electronic current of polymer electrolyte has been measured by Wagner's dc Polarization technique (17), which is used to determine the ionic and electronic charge contribution in solid polymer. An electro chemical cell has fabricated with the combination of Ag^+ /Polymer electrolyte /($\text{I}_2+\text{C}+\text{electrolyte}$) and silver (Ag) paste is coated under the constant load $100\text{K}\Omega$ as fixed small dc potential (1.5V). To get full polarized of the sample the current pass through it at least for an hour which is as shown in Fig 5.

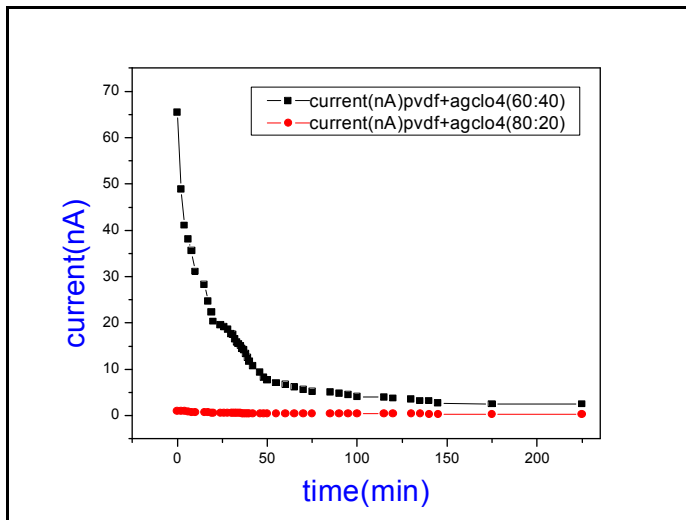


Fig. 5. Polarization current vs time plot of PVdF + AgClO₄ (60:40) PVdF + AgClO₄ (80:20)

The transference number t_{ion} is calculated by the polarization of current versus the time plot and it is calculated by initial of current by total current flows. The ionic transference number (t_{ion}) is calculated using the relation

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

The ionic transference number for all the compositions of the (PVdF + AgClO₄) electrolyte system were shown in Table 2. The total ionic transference number (t_{ion}) value is obtained at the range 0.849 – 0.961 which indicates that the charge transport in these polymer electrolyte systems is mainly due to ions and negligible electronic contribution takes place.

Discharge characteristics:

An electro chemical cell has been fabricated with the configuration of Ag/(PVdF+AgClO₄)/(I₂+C+electrolyte) for various compositions. The area and thickness of the electrolyte are respectively 1.33cm² and 100μm here Ag is act as anode whereas (I₂+C+electrolyte) working as cathode. 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.

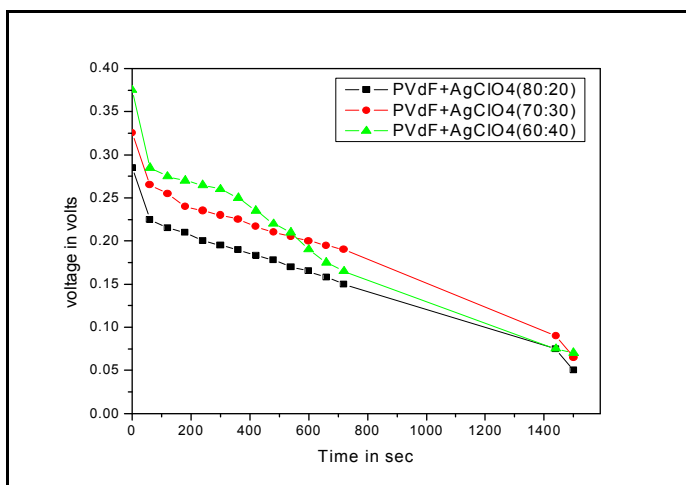


Fig. 6. Discharge Characteristics of Na/(PVdF+AgClO₄)/(I₂+C+electrolyte) Electrochemical cell for a constant load of 100 KΩ. PVdF+AgClO₄ for compositions (80:20) PVdF+AgClO₄ for compositions (70:30), PVdF+AgClO₄ for compositions (60:40).

Due to the polarization effects. Initial voltage is decreases abruptly it may be due 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) for these cells are found to be 0.285V and 0.36 mA respectively. The other cell parameters for these cells are calculated and shown in Table 3.

Table 3: Cell parameters of [PVdF+AgClO₄] polymer electrolyte cell system.

Cell parameters	PVdF+AgClO ₄ (80:20)	PVdF+AgClO ₄ (70:30)	PVdF+AgClO ₄ (60:40)
Open Circuit Voltage (OCV) (V)	0.285	0.325	0.375
Short circuit current (SCC) (nA)	0.36	0.99	0.655
Area (Cm ²)	0.5024	0.5024	0.5024
Weight (gm)	1.21	1.26	1.30
Discharge Time (h)	12	24	25
Current Density (nA/Cm ²)	0.7165	1.970	1.3037
Power Density (watt/kg)	84.7	255.3	188.94
Energy Density (watt-hr/kg)	1016.4	6127.2	4723.5

From the above figure it is observed that the combination of 60:40 (PVdF+AgClO₄) as electrolyte having higher discharge capacity. Further work aimed at obtaining higher cell capacities and specific energy is in progress.

3. Conclusions

Solid polymer electrolyte films with the combination of PVdF+AgClO₄ are prepared. IR studies confirms the complex formation of the polymer-salt. A change in melting temperature was observed on doping with AgClO₄ in PVdF. The conductivity of (PVdF+AgClO₄) (60:40) at room temperature was determined to be 4.20×10^{-5} S/cm and at 373K was increased and found to be 7.46×10^{-4} S/cm. The ionic transport number data in the PVdF+AgClO₄ solid polymeric electrolyte films indicate that the conduction is predominantly due to ions. The cell parameters evaluated worthy to fabricate for solid state battery application.

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