TechnoChem

International Journal of TechnoChem Research
ISSN:2395-4248 www.technochemsai.com
Vol.02, No.03, pp 239-243, 2016

Effect of Ammonium Salt on Structural, Conductivity and Optical Properties of PVDF Thin Film Electrolytes

A.Jayalakshmi*, A.Annapooranam, S.Sivadevi

Department of Physics, The S. F. R. College for Women, Sivakasi, Tamilnadu -626123, India

Abstract : An investigation is carried out on new solid polymer electrolytes based on Polyvinylidene fluoride (PVdF) doped with Ammonium Nitrate (NH_4NO_3), which have been prepared by solution casting technique using Dimethylformamide (DMF) as solvent. XRD analysis shows the amorphous nature of the polymer electrolytes. AC impedance analysis gives the ionic conductivity value of the electrolytes. The conductivity at room temperature (303K) has been found to be increased by the addition of ammonium nitrate and the maximum value is $1.712x10^{-5}$(S/cm) for 80%PVdF: 20% NH_4NO_3 polymer electrolyte. Dielectric study has been made to analyse the electric behavior of polymer electrolytes. From UV-Vis spectroscopy the direct band gap energy is observed to be 4.16eV & 4.08eV for pure PVdF & salt doped PVdF samples respectively.

Keywords: XRD, AC Impedance analysis, Dielectric studies, UV-Visible spectroscopy.

Introduction

The polymer electrolytes which have higher ionic conductivity play a major role in the ionic devices viz. electro chromic devices, sensors, and super capacitors[1,2]. Various polymers like PVA, PMMA, PVP, PAN, PEO and PVdF[3,4] have been used to develop polymer electrolytes. PVdF has been chosen as polymer host for the present study because of its combination of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance[5]**.** Poly (vinylidene fluoride) (PVdF) is a thermoplastic material used in a variety of products and parts such as piezoelectric film, fiber, belt, and pipe. For advanced applications of PVdF, it is highly desirable to enhance and control its physical properties such as thermal stability, mechanical modulus, and electrical conductivity[6]. Various methods have been adopted to enhance the ambient temperature ionic conductivity of the polymer electrolyte. One such method is to dissolve inorganic salt in polymer matrix. In the present work ammonium nitrate (NH_4NO_3) doped PVdF polymer electrolytes have been prepared and subjected to various characterizations such as XRD, AC impedance spectroscopy and UV-visible spectroscopy.

Experimental details

In the present study, ammonium salt doped PVdF thin film electrolytes have been prepared by solution casting technique. In this technique suitable amount of the polymer PVdF is dissolved in DMF at about 60^oC and continuously stirred with a magnetic stirrer until the solution becomes clear and transparent. Then the salt NH_4NO_3 is added and stirred well until they become homogeneous. Then the homogeneous solution is poured in poly propylene petri dishes and kept in vacuum oven for solvent evaporation at 90^oC for two days. After the complete evaporation of the solvent, the stand alone films are carefully removed from the petri dishes and sealed in an air tight cover. Samples in the concentration ratios 100:0, 90:10 and 80:20 of PVdF: NH_4NO_3 are synthesized. X-ray diffraction patterns of the prepared samples are recorded at room temperature XPERT-PRO diffractometer. AC conductivity measurements have been performed on HIOKI make LCZ meter in the frequency range 42Hz-1MHz by applying 1V, and at different temperatures ranging from 303K to 343K.

Result and discussion

X-ray Diffraction Analysis

XRD analysis is used to determine the amorphous nature of the prepared polymer electrolytes.

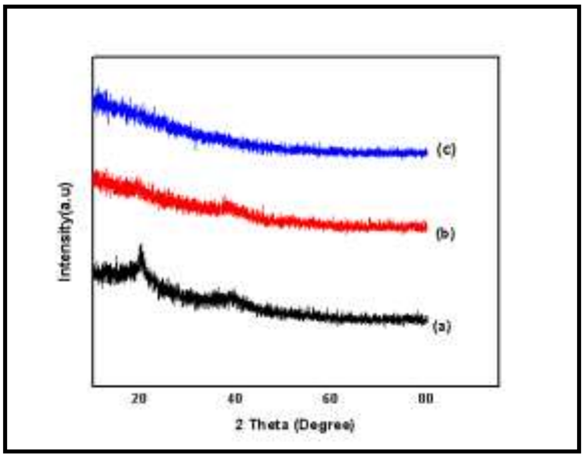
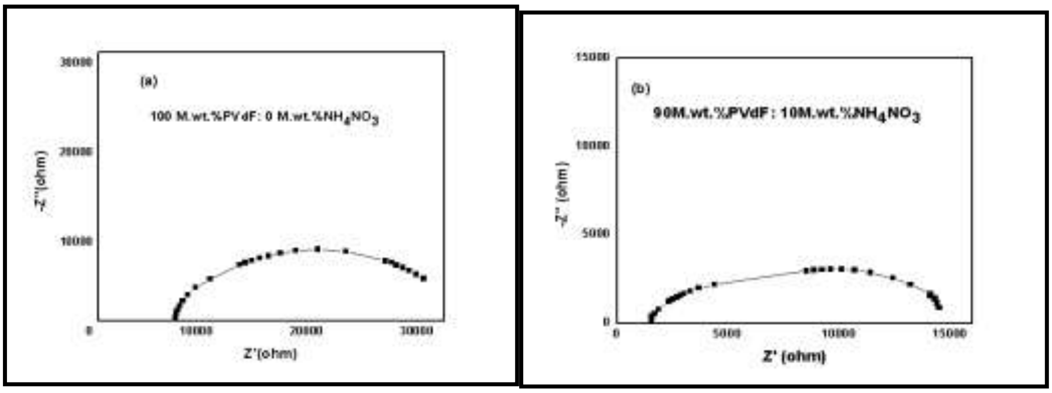


Figure 1 XRD patterns of (a) Pure PVdF, (b) 90 PVdF: 10 NH_4NO_3, (c) 80 PVdF: 20 NH_4NO_3

Figure 1 shows the typical X- ray diffraction patterns obtained for the samples for pure PVdF and PVdF doped with NH_4NO_3 in different molecular weight ratios. It has been observed from Figure1 that the broad peak around 20.3^0 corresponding to pure PVdF can be associated with the amorphous nature of PVdF[7]. The relative intensity of the broad peak decreases with increases of NH_4NO_3 concentration. This change in diffraction intensities of peak indicates that the amorphous nature of the polymer electrolytes increases with an increase in NH_4NO_3 content. The result obtained from the XRD measurements strongly suggests that there is interaction between the polymer matrix and the salt NH_4NO_3.

AC impedance Analysis

AC impedance technique is a powerful method for characterizing the electrical properties of polymer electrolytes.



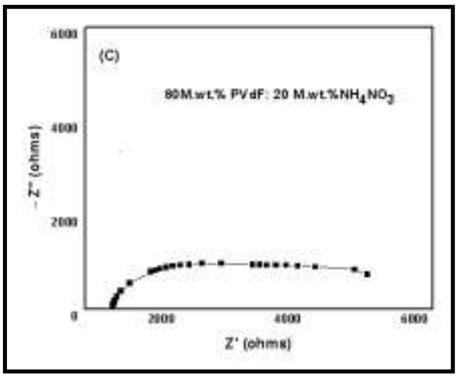


Figure 2 (a) (b) (c) show the complex impedance plot for x PVdF:(1-x) NH_4NO_3 polymer Electrolyte systems at ambient temperature (303K).

Electrical characterization of xPVdF: (1-x) NH_4NO_3 polymers have been performed using AC impedance spectroscopic technique at ambient temperature (303K) and are shown in Figure 2 (a) (b) (c). Each plot shows semicircle which is due to the bulk effect of the electrolytes. The bulk resistance (R_b) of the electrolytes can be obtained from the intercept of the high frequency semicircle on the Z' axis[8]. It can be observed from the plots that as the concentration of salt increases, the diameter of the semicircle decreases implying the decrease in bulk resistance. The ionic conductivity of the polymer electrolytes can be calculated using the equation

$\sigma = l/R_bA$

where, l and A are the thickness and area of the electrolyte film respectively. R_b is the bulk resistance of the electrolyte. The highest ionic conductivity at ambient temperature has been found for the 80 M.wt % PVdF : 20 M.wt % NH_4NO_3. The conductivity values measured for x PVdF: (1-x) NH_4NO_3 polymer electrolytes prepared at room temperature are presented in Table1.

Table 1 Ionic conductivity values for x PVdF: (1-x) NH_4NO_3 at room temperature.

Sample x PVdF: (1-x) NH_4NO_3	**Conductivity (Scm^{-1})**
100:0	1.966×10^{-7}
90:10	8.89×10^{-7}
80:20	**1.712×10^{-5}**

Dielectric spectra Analysis

The study of dielectric properties is essential because it gives valuable information about the loss of energy (**ε''**) and dielectric constant (ε').

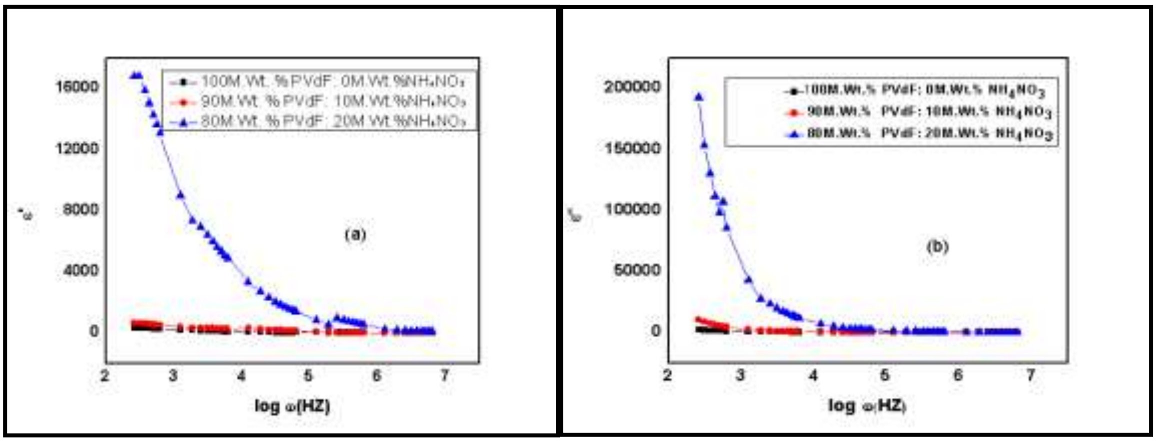


Figure 3 Frequency dependence of (a) ε'(ω) for x PVdF : (1-x) NH_4NO_3 systems Frequency dependence of (b) ε''(ω) for x PVdF : (1-x) NH_4NO_3 systems at room temperature.

The dielectric behavior of the polymer electrolyte system is described by using the dielectric function ε* is defined by,

ε*= ε' (ω) - iε'' (ω)

where ε'(ω) is real component which tells about the storage of energy in each cycle of the applied electric field and ε''(ω) is imaginary component which tells about the loss of energy in each cycle of the applied electric field. Figure 3 (a) (b) shows the frequency dependence of real ε'(ω) and imaginary ε''(ω) parts of dielectric function (permittivity) of various composition of PVdF with ammonium nitrate at room temperature. It was observed that the dielectric constant and dielectric loss decreases with increasing frequency. The dipole move along the electric field at low frequencies and at high frequencies they cannot move resulting in a constant value. At low frequencies the dispersion of real and imaginary part of permittivity is due to space-charge polarization which is observed for all compositio[9]. High values of **ε'**and **ε''** have been obtained for the highest conducting sample 80%PVdF: 20%NH_4NO_3.

UV-Vis spectral analysis

The UV-visible absorption spectroscopy technique is used for the investigation of optical properties of the synthesized polymer electrolytes.

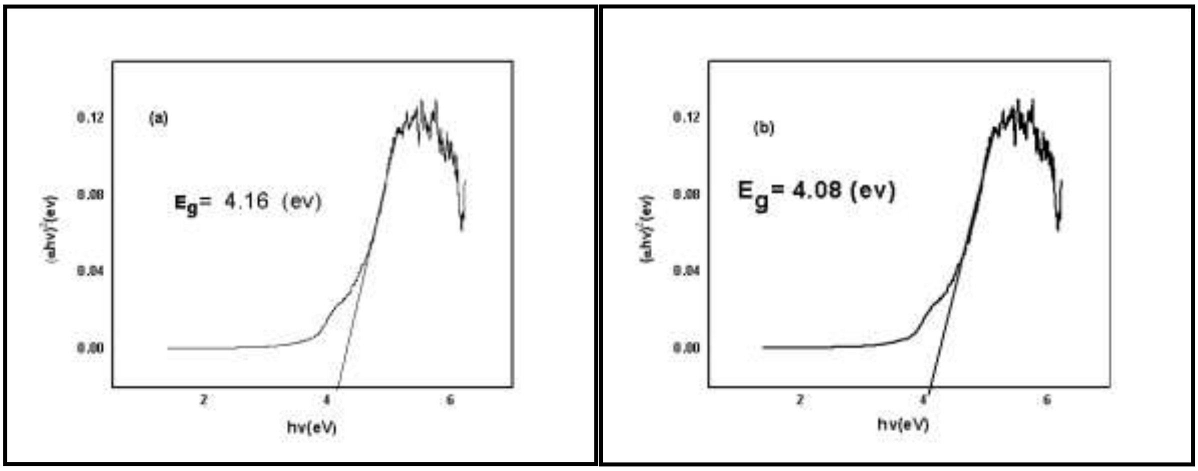


Figure 4 (a) (b) UV-visible spectra for pure PVdF and 80%PVdF: 20%NH_4NO_3.

Figure 4 (a) (b) shows a plot of $(\alpha h\nu)^2$ versus photon energy (hν) for pure PVdF and 80% PVdF:20%NH_4NO_3[10] , where α is the absorption coefficient, h is the Planck's constant and ν is the photon energy. The band gap energy is calculated from the plot by extrapolating the straight line portion of the curve to zero absorption coefficient value. The value thus calculated is equal to 4.16 eV for pure PVdF and 4.08 eV for 80%PVdF: 20% NH_4NO_3.

Conclusion

PVdF based polymer electrolyte with different concentration of ammonium nitrate have been prepared by solution casting technique. The XRD analysis reveals the increase in amorphous nature of the polymer PVdF with the increase of NH_4NO_3 salt concentration. The polymer electrolyte having 80 % PVdF: 20% NH_4NO_3 has low bulk resistance and high conductivity of **$1.712x10^{-5}$ S/cm** (from cole- cole spectra) at **303 K.** Dielectric Spectroscopy has been carried out to analyses the dielectric behavior of polymer electrolyte. The optical band gap for pure PVdF and 80% PVdF: 20%NH_4NO_3 - are calculated and it is found that the band gap energy is slightly decreased with the addition of NH_4NO_3.

References:

1. MacCallum JR, Vincent CA (eds) Polymer electrolyte reviews 1 and Elsevier, London, 1987 and 1989
2. Scrosati B (ed) Applications of electro active polymers. Chapman & Hall, London, 1993
3. Hirankumar G, Selvasekarpandian S, Kuwata N, Kawamura J,Hattori T J Power Sources., 2005, 144-262.
4. Sivadevi S, Selvasekarapandian S, Vijaya N, KingslinMaryGenova F, Sanjeeviraja C, Structural and AC Impedance Analysis of Blend polymer electrolyte based on PVA and PAN .International Journal of Scientific Research.,2013,2.
5. Tran M, Shaffer M and Bismarck Manufacturing Carbon Nanotube/PVdFNanocomposite Powders. Macromol.Mater. *Eng*., 2008, 293; 188-193.
6. Devikala S, Kamaraj P, Arthanareeswari M. PVdF –TiO_2 Composite as a corrosion Inhibitor for Mild steel in 3.5% NaCl. International Journal of Advanced Chemical Science and Application. 2014, 2.
7. Yu S, Zheng W, Yu W, Zhang Y, Jiang Q and Zhao Z Formation Mechanism of β- Phase in PVdF/CNT Composite Prepared by the Sonication Method. Macromolecules.2009, 42; 8870-8874.
8. Boukamp BA Solid State Ionics. 1986, 20-301
9. Ramesh S, Arof AK Ionic conductivity studies of plasticized poly(vinylchloride) Polymer electrolytes. Mater sci Eng., 2001, 85; 11-15
10. Ali Akbar Yoursefi, Influence of Polymer Blending on crystalline structure of Polyvinylidene Fluoride. Iranian Polymer Journal, 2011, 20(2); 109-121.

*****