

Structural and Dielectric Behaviour of Plasticized Gel Polymer Electrolyte Based on PVDF

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Abstract

In the present work, the improvement in ion transport behavior of polyvinylidene fluoride (PVdF) - based polymer electrolytes have been investigated using different types of fillers. The effects of different fillers on structural and electrical behavior of electrolyte were studied by different experimental tools like XRD, Optical technique, impedance spectroscopy and dielectric relaxation measurements. Argand plots show dispersive nature of relaxation time or in homogeneously space charge polarization of the nanocomposite polymer electrolyte.

Keywords:

Ionic conductivity, Polymer composite electrolyte, Plasticizer, Polymer salt interaction, PVDF

Introduction

Nano composite polymer electrolytes have received considerable attention because of their potential application in electrochemical devices like fuel cell, rechargeable battery etc [1-5]. PVdF is a very attractive polymer having piezoelectric and pyroelectric characteristics. It is an acid resistant, inert, semi crystalline polymer that is extensively used in electronic devices like sensors, transducers etc. as well as in biomedical application. PVdF is a linear fluorinated hydrocarbon with the repeat unit ($\text{CH}_2\text{-CF}_2$). PVdF chains have a net dipole moment pointing from the electronegative fluorine to electropositive hydrogen producing a net dipole moment nearly perpendicular to the polymer chain having four different polymorph. The polymer electrolyte based PVdF is most useful due to strongly electron withdrawing functional group with high dielectric constant. The high ϵ is effective in dissociating the salt to produce a large number of charge carriers for conduction. The use of plasticizer namely ethylene carbonate (EC) & polypropylene carbonate (PC) facilitate high solubility conduction through the swollen PVdF is highly credible. In order to modify the physical properties and protonic behaviour of PVdF based film the addition of ceramic /organic fillers are a novel technique. A number of composite polymer electrolyte systems have been investigated using the variety of polymers with fillers [6]. In general, fillers are classified into two broad groups, the active and passive filler {6}. The addition of filler have the special relevance is due to Lewis acid – base interaction between the filler and component of the polymer electrolyte [7-9]. The aim of the present communication is to investigate the effect of different filler groups on the structure and ionic conductivity of plasticized PVdF solid polymer electrolyte.

Experimental

Poly(vinylidene fluoride) (PVdF; Aldrich sigma) with an average molecular weight of ($\sim 5.34 \times 10^5$), Ammonium acetate ($\text{CH}_3\text{COONH}_4$; Ranken India), and different groups of filler i.e. Oxide filler (namely SiO_2 , TiO_2 , Al_2O_3 and multi oxide Fly Ash), Carbon group (i.e. graphite and MWCNT), Lithium ferrite and multiferroic filler BFO, Ethylene carbonate [(EC) Alfa Sigma MW~88.06g/mol] and Propylene carbonate [PC, Alfa Sigma MW~102.09g/mol] in the volume ratio of 1:1 is used as plasticizer were used for the preparation of the polymer electrolyte. Distilled Tetrahydrofuran (THF) in a suitable ratio were used as common solvent. The dissolved polymer solution, plasticizers and salts were mixed together and the solution was stirred continuously to obtain a homogenous mixture. The solution was allowed to evaporate very slowly until the gelly state obtained. The gel was allowed to

dry in normal ambient and obtained a gel film for further study. We have prepared the following groups of NCPEs:

- (I) 30[90 PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC]
- (II) 99{30[90 PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC]} +1{LiFerrite}
- (III) 99{30[90 PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC]} +1{CNT or Graphite}
- (IV) 99{30[90 PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC]} +1{BFO}
- (V) 99{30[90 PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC]} +1{FlyAsh, SiO₂, TiO₂ and Al₂O₃}

Structural studies of these gel films were analyzed by optical measurement for the film morphological studies and optical micrographs were taken by Lica Polarising Microscope, XRD (Philips Expert Model) using CuK α ($\lambda=1.542\text{\AA}$) in the Bragg's angle range ($2\theta=15-60^\circ$) were carried out to investigate the complexation behavior. The electrical conductivity behavior was measured from impedance plot at different temperature using LCZ meter (HiokiLCR 5320, Japan) in the frequency range (40-100 KHz).

Result and Discussions

The x-ray diffraction pattern of different groups 30[90 PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC] and gel electrolyte system namely; 99{30[90 PVdF+10(NH₄)₂COOCH₃]:70[EC+PC]}+1{LiFerrite}, 99{30[90 PVdF+10(NH₄)₂COOCH₃]:70[EC+PC]}+1{CNT}, 99{30[90PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC]} +1{BFO}, 99{30[90 PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC]} +1{FlyAsh} are shown in figure -1. The comparative look of the main characteristic peak of PVdF was observed at 20° . After the addition of salt and filler, it was noted that the broadness of the main peaks increases in all groups of fillers. The intensity of the peak is also tending to downsizing in all groups of filler. It is clear to be that the broadness of the 20° peak (i.e.the main peak of PVdF) with the flyash filler (oxide group) is found maximum. These observations apparently show that polymer undergoes structural reorganization after adding the salt, Plasticizer and filler. The increase in broadness of XRD peak is an indication of the polymer /salt / interaction [10].

The optical micrograph of different 30[90 PVdF+10(NH₄)₂COOCH₃]: 70[EC+PC] gel electrolyte system were recorded to assess the morphology of gel electrolyte in figure-2. From the figure it is clear that the porous structure of the host polymer is maintained after the interaction of salt / filler of different groups. The pore size in the matrix is relatively low in case of ferrite filler with respect to the oxide and carbon based filler. In the oxide group of filler increase in number of pore size is also recorded.

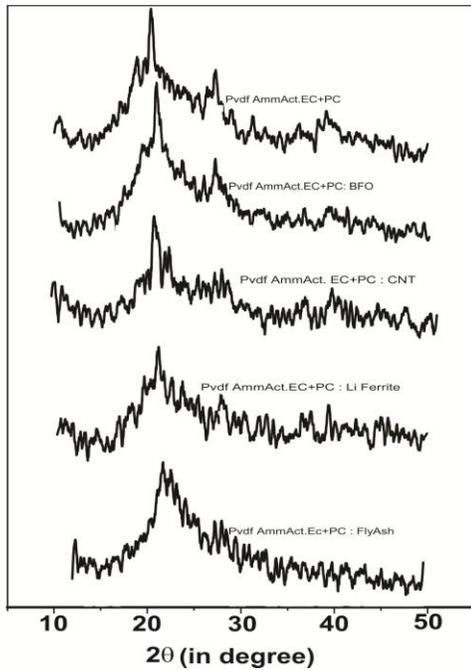


Figure:1 XRD pattern of different nano Composite polymer electrolyte

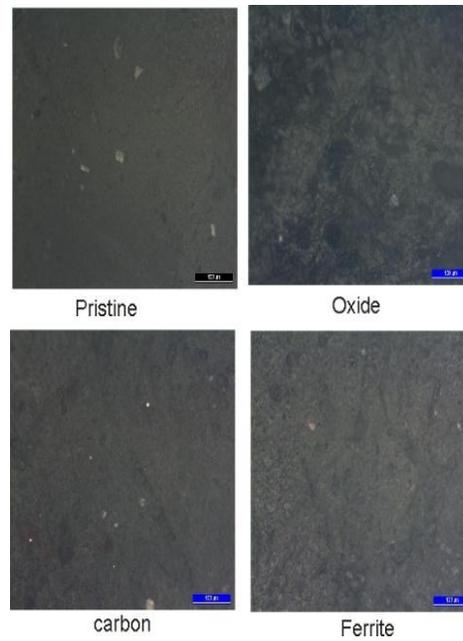


Figure:2 Optical micrograph of different nano Composite polymer electrolyte

The ionic conduction patterns in this electrolyte system were carried out by the impedance measurement methods. The change in conductivity with frequency at different temperature in all five type of system are shown in figure- 3(a) to, conceive the relaxation dynamics in terms of conductivity spectra at different temperature, the conductivity is scaled using Ghosh's Scaling Method. Scaling of conductivity were carried out by the following method at three representative temperature 35, 55, 80°C

$$\sigma / \sigma_0 = F (f$$

/f₀)
(1)

where, f₀ is the characteristics frequency. The scaled conductivity with scaled frequency is shown in figure-3(b) shows that master curves of all the models have superimposition in ac conductivity frequency range governed by hopping conduction. In the temperature dependence conductivity with frequency it clearly shows that σ increases with frequency give a plateau and finally increases sharply (at higher frequency). This type of nature suggests that change in conductivity follows the universal power law.

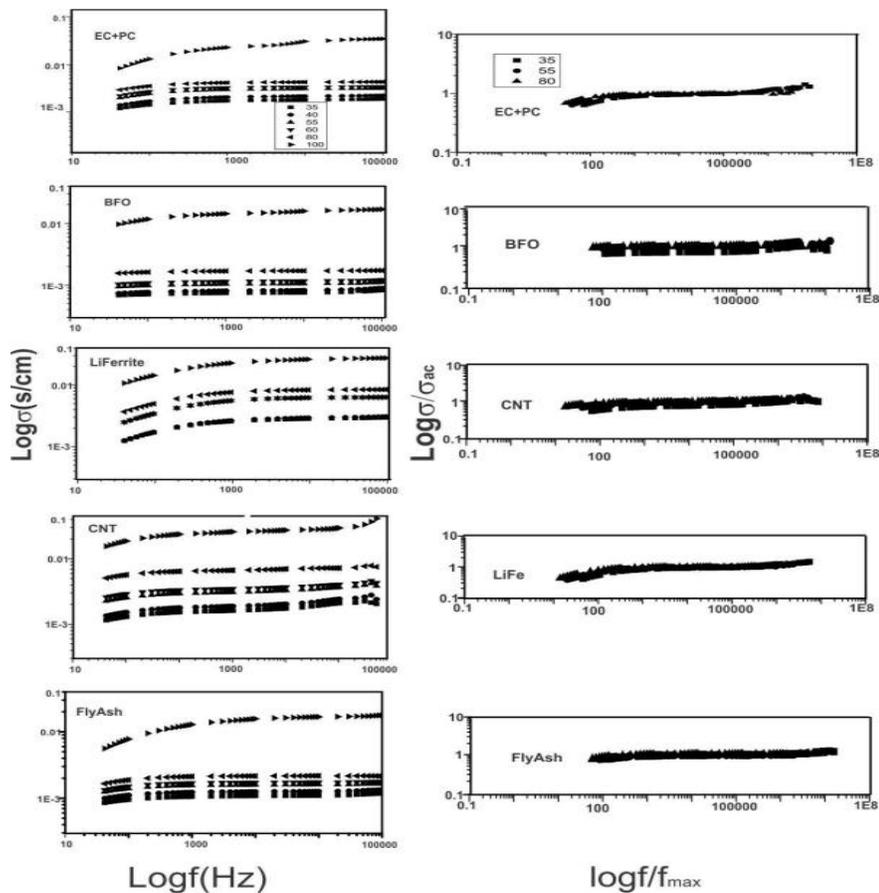


Figure:3 Conductivity scaling of different nano Composite polymer electrolyte

In ferrite based polymer composite electrolyte with ferrite filler and multi ferroic system (BFO) the scaled conductivity does not give the ideal overlapping throughout the complete scaled range of frequency but in other three group all the conductivity are overlapped in a single master curve with high dispersion in low frequency range. This indicates that the mechanism of conduction is same as in the complete temperature range of study the low frequency dispersion is possibly due to electrode polarization.

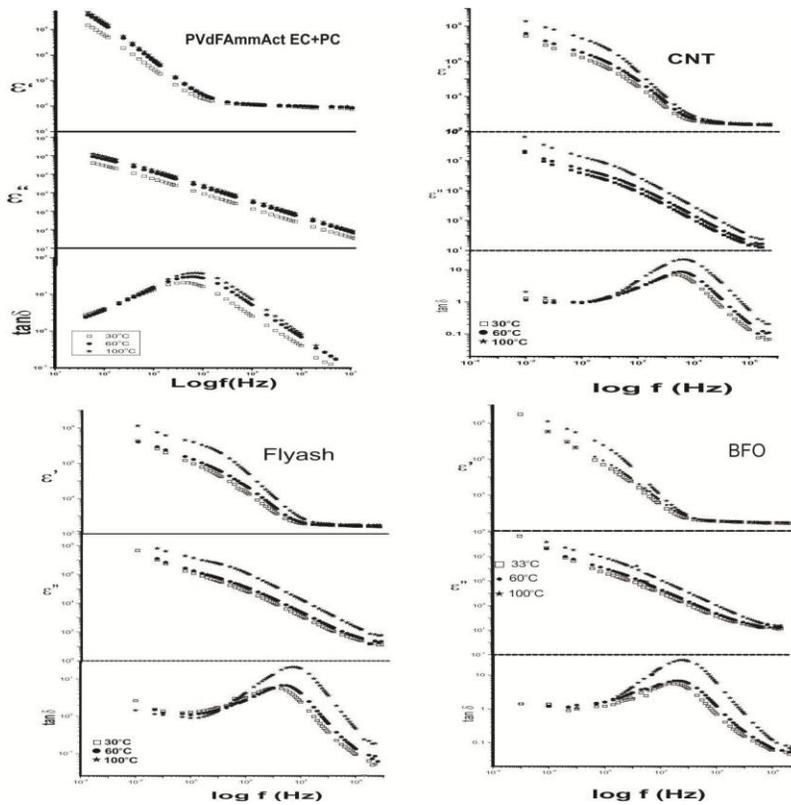


Figure:4 Dielectric parameters of different nano composite polymer electrolyte

To study the master curve of dielectric parameter we have also used the three temperatures shown in figure-4. The master curve representation of various dielectric parameters (ϵ' , ϵ'' , & $\tan\delta$) with frequency is a unique method of representation of dielectric behavior. In a pristine electrolyte system the variation of dielectric loss is linear, but with the addition of filler, this nature changes and some relaxation peaks are also observed. The dielectric constant curve shows the dispersive nature at low frequency range. It is also observed and

peak shift in the higher frequency side with the temperature.

Conclusions

From the results obtained in this work, it can be concluded that the gel polymer electrolyte system shows a significant improvement in stability and ionic conductivity, which is beneficial for the application of electrochemical devices. In these electrolytes, filler particles are dispersed in the polymer matrix and retain the original porous structure. The enhancement in the

conductivity as well as dielectric behavior of the composite electrolyte in the filler based, is due to the intercalation interaction of the fillers i.e. Lewis acid base interaction between the carrier and the porous matrix of polymer

varying the activity of the carrier as well as its tendency to migrate in the interporous space. The study of the temperature dependence of ϵ' , ϵ'' , $\tan\delta$, σ_{ac} , σ_{dc} showed a dielectric dispersion.

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