Journal of Nanoscience and Nanoengineering
Vol. 1, No. 4, 2015, pp. 265-270
http://www.aiscience.org/journal/jnn

Study of Phase Crystallinity Effect on Ionic Behaviour of PVDF Based Nanocomposite Membrane

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Abstract

A nanocomposite polymer electrolyte can be synthesised with polymer, plasticizer, salt and filler for the device as well as biomedical applications. These gel electrolytes have considerably high ionic conductivity at room temperature. In present work, a PVDF based gel electrolyte has been synthesized and characterized. Ammonium acetate is used as salt or dopant and Ethylene Carbonate (EC) with Propylene Carbonate (PC) as a plasticizing solvent. Graphite is dispersed as the third component i.e. filler. The nanocomposite gel electrolyte was synthesized by phase inversion technique. The aim of the present communication is to investigate the possible application of the nanocomposite polymer electrolyte in electrochemical devices.

Keywords

Ionic Conductivity, Plasticizer, Polymer Salt Interaction, PVdF, NCPEs Etc

1. Introduction

The applications of gel electrolyte in variety of electrochemical devices e.g. rechargeable lithium batteries, sensors, solar cells, display devices etc. [1-4] are common,due to their special type of three dimensional network structure. Poly Vinyldienefloride (PVdF) polymer has drawn the attention of scientific communities due to its piezoelectric behavior with acid resistant chemically inert and mechanically strong nature that has been used in various device and biomedical applications [5-8]. PVdF is a semicrystalline polymer, can be processed by phase inversion technique into micro porous membranes that encompass a wide spectrum of surface morphology. The typical advantages of organic polymers are flexibility, toughness, formability and low density. PVdF exhibits five different crystalline phases known as: form I (β) form II (α) form III (γ) polar II (α_p) and polar form III (γ_p) [9]. Form I is distinguished from the others by very important properties for application. The PVdF is a typical type of polymer for the gel formation. To improve their processability and mechanical properties, addition of plasticizer is a novel route. Additions of plasticizer serve to decrease the intermolecular force between the polymer chains, resulting in a lowering the melting point, softened and flexible polymer matrix. Use of combination of plasticizers (e.g. combination of Ethylene Carbonate (EC), Propylene Carbonate (PC) in 1:1 molar ratio) show the better result [10-11]. Ammonium acetate ($C_2H_7NO_2$) is used as a dopant salt because it is easily dissociable (in presence of water) and very much useful for the medical use like DNA extraction [12]. The addition of carbon filler i.e. graphite provides moderately high surface area which leads to excellent performance of composite polymer electrolyte in terms of conductivity and interfacial stability. Graphite has additional advantages including increased electrical and thermal conductivity so if one can effectively disperse

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graphite in a polymer composite many additional properties such as conductivity and electromagnetic resistance can be improved [13-14]. Prompted by these considerations, the present work has been carried out to synthesize and characterize PVdF based polymer gel electrolyte. This electrolyte is characterize for ionic conduction using different experimental tools.

2. Experimental

Poly (vinylidene fluoride) (PVdF; Aldrich sigma) with an average molecular weight of ($5.34x10^5$), Ammonium acetate (CH_3COONH_4; Rankem India), and Graphite filler, along with plasticizer mixture of Ethylene carbonate [(EC) Sigma MW 88.06 g/mol] and Propylene carbonate [PC, Sigma MW 102.09 g/mol] were used for the preparation of the polymer electrolyte. Distilled Tetrahydrofuran (THF) in a suitable ratio was used as common solvent. The dissolved polymer solution, plasticizers and salts were mixed together and the solution was stirred continuously to obtain a homogeneous mixture. The solution was simultaneously allowed to evaporate very slowly until the gelly state was obtained. The gel was poured in petridishes to dry in normal ambient to obtain the standing gel film for further studies. Following NCPE was prepared for characterization:

1. $(PVDF_{0:9}+((NH_4)_2COOCH_3)_{0:1})$
2. $[(PVDF_{0:9}+((NH_4)_2COOCH_3)_{0:1})_{0:3}$: $(EC+PC)_{0:7}]$
3. $[(PVDF_{0:9}+((NH_4)_2COOCH_3)_{0:1})_{0:3}$: $(EC+PC)_{0:7}]_{0:99}$ $+[Graphite_{0:01}]$

Structural and morphological aspects were studied by X-ray diffractometer (XRD) (Philips X'pert Model) using $CuK_\alpha(\lambda=1.542Å)$ in the Bragg's angle range (2θ) = 15-50° and infrared spectrogram (Brucker Alpha Infrared Spectrophotometer, Germany) was used to investigate the complexationbehavior. To study the β-phase crystallinity, polymeric films were annealed at different temperatures (i.e. 70, 90, 130 and 160°C). UV Visible spectrophotometer (systronics 2201) is also used to understand the behavior of NCPE. The electrical conductivity and dielectric response was measured from impedance plot at different temperature using LCZ meter (Hioki LCR 3520, Japan) in the frequency range (40-100 KHz).

3. Results and Discussion

The x-ray diffraction pattern of pristine ($PVDF_{0.9}$: $((NH_4)_2COOCH_3)_{0.1})_{0.3}$: $(EC+PC)_{0.7}$ and composite electrolytes containing graphite fillers [($PVDF_{0.9}$: $((NH_4)_2COOCH_3)_{0.1})_{0.3}$: $(EC+PC)_{0.7}]_{0.99}$: $Graphite_{0.01}$ is shown in Figure 1.

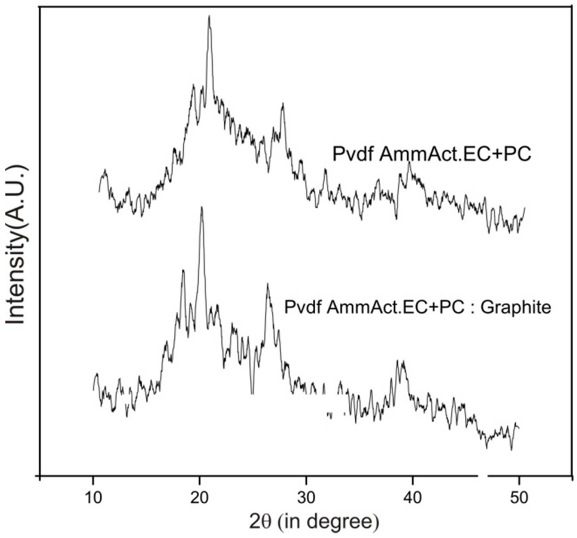

Figure 1. XRD pattern of pristine and composite electrolyte.

In the XRD curve of pristine sample the main peaks are at 2θ =20.3° (101), 17.6° (100), 18.4° (020) and 26.6° (021)[15]. The peaks 17.6° and 18.4° are indication of α-phase. The most intense peak at 20.3° (is a γ phase peak) with other neighboring 20.7° and 20.8° confirm the β-phase in the PVdF polymer matrix[16]. In the spectrum of composite electrolyte it was noted that the broadness of the main peak is increased and the intensity tried to downsize after the dispersal of filler (i.e. graphite). The main characteristic peak of graphite is present at 26.54°[17]. The effect of interaction of graphite with pristine electrolyte is clearly visible in the spectrum. Thesharpness of two peaks 26.5° and 39.2° became more intense than the earlier. It suggests that C-C bond of graphite is not undermined by interaction or oxidation. The increase in broadness is a clear indication of more amorphousity. The degree of crystallinty of these two films were calculated using the equation [18]

$$X_c = \frac{I_c}{I_T} x100\%$$

Where I_c is the area, under the crystalline peaks at 2θ =20.3°, 26.6° and 39.2°, I_T is the total area under the diffractogram from 2θ=15-50°. The average crystallinity of both films were calculated and found nearly equal (~ 41%), which is less than pure PVdF electrolyte. This implies that the less crystallinity is favorable for better ionic conductivity. Using the Scherrer's formula [19] the calculated average crystallite size is 40-50 nm.

The FTIR spectrum of PVdF, EC, PC and Ammonium Acetate salt is shown in Figure 2(i). In this figure the main vibrational peaks at 1381,1230 & 840cm^{-1} are of PVdF, 2325&1021cm^{-1} are of ammonium acetate, 1178&977cm^{-1} are due to EC, and 1397& 1060cm^{-1}are PC related peaks. The IR spectrum after the complexation of polymer/salt/filler is also shown in same figure. In these spectrums, it is clearly observed that the intensity of main peaks of PVdF (EC+PC) is reduced after the interaction with salt as well as the filler, the prominent peaks and their assignments are listed in Table 1. The figure 2(ii) is the enlarge view of spectrum in the frequency range 840cm^{-1} to 700cm^{-1} for the clear demonstration of two characteristic peaks 840cm^{-1} (β-phase) and 763cm^{-1} (α-phase) of the PVdF polymer. The quantitative determination of different PVdF polymorph content was determined with the help of FTIR Spectroscopy. The β-crystalline (phase) content in the different composites was calculated using the following equation [20]

$$F_\beta = \frac{A_\beta}{1.26A_\alpha + A_\beta}$$

Where A_α and A_β corresponds to the height of absorption band 763 and 840cm^{-1} respectively. In the present case peak heights (areas) of 763cm^{-1} (α-form) and 840cm^{-1}(β-form) were used for the above calculation.

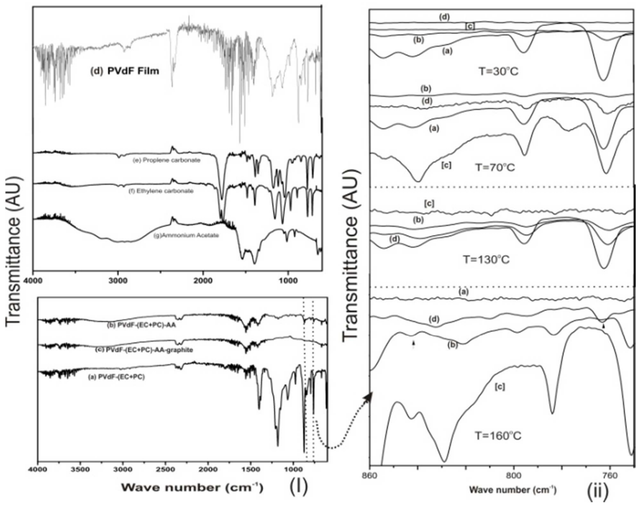

Figure 2. FTIR spectra of (i) different components of composite electrolytes and (ii) enlarge view of spectrum in the wavenumber range 860 cm^{-1} - 700 cm^{-1}.

Table 1. Prominent Infrared peaks and their assignments where *A*:PVdF-[EC-PC] Film/Powder, *B*:PVdF-[EC-PC] Ammonium Acetate Film and *C*:PVdF-[EC-PC] Ammonium Acetate-Graphite Film.

A **(cm^{-1})**	***B*** **(cm^{-1})**	***C*** **(cm^{-1})**	**Interpretations**
3028			- CF stretching vibration
2980			- C-H symmetric stretching vibration
2920			- γ (CH)
2852			- C-H asymmetric stretching vibration
	2325		-ammonium Acetate related peak
	1559	1555	- symmetric γ(-NH_3^+) band
1502	1505	1506	C=O bond
1399	1397	1400	in plane bending or scissoring of CH_2 group
1381			-C-O stretching
1338	1340	1334	-CH_3 deformation
1213	1208		- CF wagging vibration/ C-O stretching
1181	1178	1178	- CF stretching vibration
1152	1142		-CH_2 wagging
1068	1060		-C-C skelton vibration
	1021		-ammonium Acetate related peak
970	977		-EC related peak
869	870		-α or γ phase of PVdF
839	837		-β phase
792	793		In plane bending or rocking vib in α-phase
763	761		Crystalline α-phase
668	667	668	α-phase, head to head (h-h) and tail to tail (t-t) defects
610	611	612	-CF_2 Bending

The change in β-crystallinity after the modification (due to salt and filler) of polymeric matrix also affect the overall amourphisity of the system. The composite systems with salt show the reduction in β-crystalline (phase) content. This decrease favors the better conduction. But the dispersal of fillers tries to enhance crystalline values. A comparative study of the β-crystal content with conductivity is explained in next section. In order to better understanding the behavior of NCPE, we have recorded the UV spectrum of the pristine and composite electrolyte system (Fig. 3).

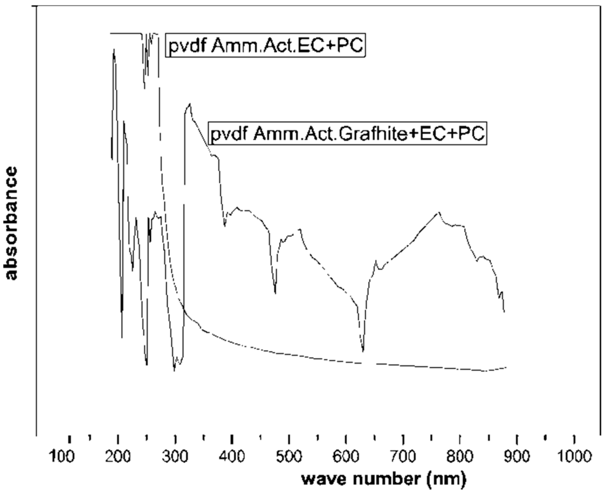

Figure 3. UV spectra of pristine and nanocomposite electrolytes.

UV absorption spectrum of PVdF based pristine film shows a sharp decrease in the range (280-310 nm) and then gradually decrease slowly in the higher wavelength side[21]. In pure PVdF two distinct peaks present at 320 nmto 360 nm (characteristic peak) may be correlated with electronic transition in fluorocarbon ions but after complexation these peaks shift in the lower side. After 360nm absorption decreases linearly at higher wavelength.In the film with salt i.e ($PVDF_{0.9}$: $((NH_4)_2COOCH_3)_{0.1})_{0.3}$: $(EC+PC)_{0.7}$ shows the shift in the peak toward the downside, means the insertion/interaction of $(NH_4)_2COOCH_3$ in the polymer chain of PVdF modified by the EC/PC. In the higher wave number no change occurs in the linearity of spectrum. But the dispersal of graphite as filler completely disturbs the structure. In the UV spectrum of $[(PVDF_{0.9}$: $((NH_4)_2COOCH_3)_{0.1})_{0.3}$: $(EC+PC)_{0.7}]_{0.99}$: $Graphite_{0.01}$ some prominent peaks observed the lower wave number peaks 232 and 340nm is possibly due to interaction of polymer–salt–filler interaction. Other peaks 650 and 950nm is an indication of formation of graphite oxide. Similar results are also reported by other authors [22].

The a.c. conductivity of the electrolyte has been evaluated using the relation

$$\sigma_{ac} = \epsilon' \epsilon_o \omega tan\delta$$

whereϵ_o is the permittivity in vacuum and ω is the angular frequency. Variation of a.c. conductivity with frequency at different temperatures for $(PVDF_{0.9}: ((NH_4)_2COOCH_3)_{0.1})_{0.3}: (EC+PC)_{0.7}$ and $[(PVDF_{0.9}: ((NH_4)_2COOCH_3)_{0.1})_{0.3}: (EC+PC)_{0.7}]_{0.99}$: $Graphite_{0.01}$ film is shown in Figure 4. The conductivity of the NCPE film increases slowly with increasing frequency at different temperatures. This temperature independent relaxation dynamics of the system thus suggest that the a.c. conductivity (σ_{ac}) of the samples depends on the frequency.

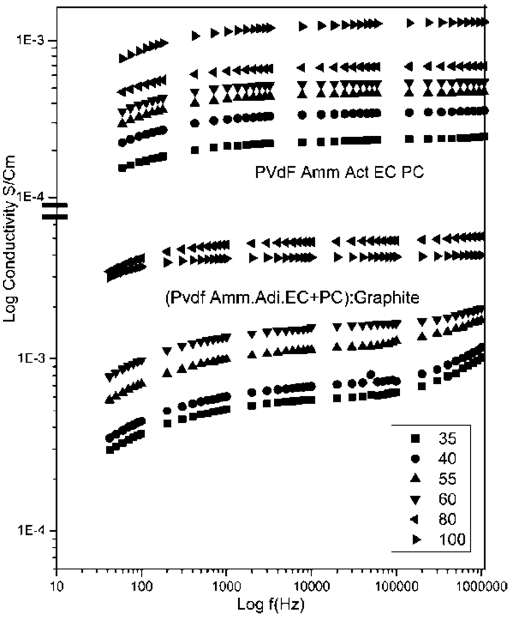

Figure 4. Variation of conductivity with frequncy at different temperature in pristine and nanocomposite electrolytes (in inset scaled conductivity with scaled frequency at different temperature is shown).

The frequency dependent conductivity at various temperatures has similar resemblance with the typical nature of conductivity in the polymer electrolyte. At all the temperatures conductivity follow the universal power law. To observe the conduction dynamics, the scaled value of conductivity is plotted with frequency at various temperature (Figure 4 (inset)). It is apparent that scaled conductivity spectra of pristine electrolyte sample try to coincide with minor aberrations, but in the nanocomposite polymer electrolyte, scaled conductivity spectra at different temperature merge on a single master curve in the complete frequency range (40Hz-100KHz). This type of process is called "Time-temperature superimposition principle"[23]. The method of scaling is usually adopted to scale thedifferent data sets into a master curve in order to get common underlying behavior. It implies that the relaxation dynamics upon addition of graphite filler changes and forced to follow similar relaxation dynamics at all temperatures in this range. In Figure 5, we compare the change in bulk electrical conductivity with PVdF β-phase content composition in the composite polymer electrolyte films. In the temperature dependence of conductivity, up to a limited temperature range (Range-I, RT–70°C), it increases linearly and follows an Arrhenius type thermally activated process, then it proceed according to VTF type process (Range-II, 70–100°C). At higher temperature the conductivity is very low and difficult to measure by Hioki LCZ-3532 instrument. The dispersal of filler tries to decrease the bulk conductivity at higher temperature in nanocomposite polymer electrolyte. The change in β-phase content composition with temperature show initial decrease in two composite electrolyte, then increase (upto 160°C), but in the graphite dispersed NCPE initial increase is followed by a decrease. It means the decrease in crystalline content is better for increase in conductivity. This phenomenon is visible in the temperature dependence of conductivity. The dissimilarity in NCPE with respect to other two electrolytes is clearly linked with the morphological disturbance recorded in UV-spectroscopic studies.

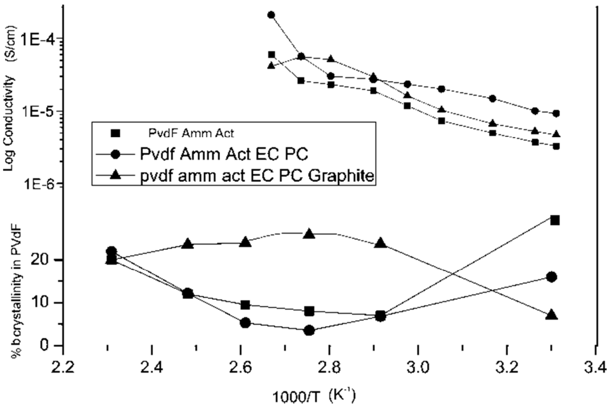

Figure 5. Variation of conductivity and β-phase crystalline content with different temperatures in different electrolytes.

We have studied the electrochemical window of pristine and nanocomposite electrolyte by the cyclic voltametry (CV) in the potential range -8V to 8V. CV curve shows that graphite based NCPE has good electrochemical window stability is more than ±4.5 volts. It can be seen from voltagram that the voltage of pristine polymer electrolyte is around ±2.0 volts. Thus electrochemical window for graphite based NCPE is seen to increase by ±2.5 volts with respect to pristine electrolyte.

The change in relative dielectric constant of composite polymer electrolyte with frequency and different temperature is given in Figure 6. A strong frequency dispersion in relative permittivity (ϵ') were recorded in low frequency region followed by a nearly frequency independent nature at higher frequencies above 10 KHz in the pristine sample. Such a feature is observed typically in polymeric electrolyte substance. The decrease of ϵ' with increasing frequency may be attributed to electrical relaxation or inability of dipoles to rotate rapidly leading to a lag between frequency of oscillating dipoles and that of applied field. As the frequency increases the ionic and orientation source of polarizibility decreases and finally disappeared due to inertia of mobile ions and we get constant value of dielectric constant. Another important fact noticed after the dispersal of filler a peak observed around the 2 kHz frequency at higher temperature i.e. 60°C & 100°C. These relaxation peaks are possibly due to electrode interfacial polarization. A specific peak is observed in the tangent loss at 100°C, which is possibly due to the interaction of filler with polymer-salt matrix. The UV study shows that the dispersal of filler in the pristine electrolyte is a possible reason of slight increase of crystallinity, also a cause of formation of molecular dipoles. The entire response reflects a non-Debye relaxation in composite electrolyte system. Similar phenomenon observed in the tangent loss behavior of the electrolyte with filler at higher temperature.

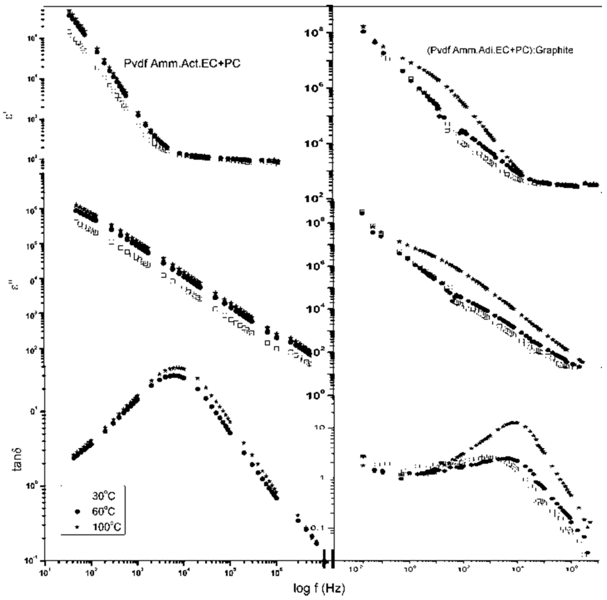

Figure 6. Variation of dielectric function with frequncy at different temperature in pristine and nanocomposite electrolytes.

4. Conclusion

PVDF based gel electrolyte were prepared by phase inversion technique. All electrolytes show appreciable conductivities (with two order enhancement in NCPE) even at room temperature. Experimental studies show that the graphite as filler modifies the physical and morphological behavior and provide higher amorphosity in nano composite electrolyte. The XRD observations confirm formation of nano composite system. Further graphite nano-particles are able to change original bonding behavior of PVDF. From FTIR it is observed that β-crystal content is an indication of amourphisity of the polymeric matrix. The decrease in β-crystal content enhance the amorphous region this is favorable for the better conduction. The increase and decrease in conductivity with salt concentration has been explained with help of ion association and dissociation effect in PVDF chain.CV result show that NCPE has good reversibility and window stability between ±4.5volts. In the dielectric relaxation behaviour shows, electrode polarization/ interfacial polarization effect is seen in the NCPE.

Acknowledgement

Thanks to SERB, Dept. of Science and Technology, Govt. of India for providing the financial support for this work in a form of research grant.

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