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Electric and Dielectric Properties of Sodium Ion Conducting Polymer Electrolyte

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ABSTRACT

Polymer electrolyte based on Poly(vinylidene fluoride-co-hexafluropropylene) (P(VdF-HFP)) and sodium triflate (NaTf) was prepared and its ionic conductivity was found to be 4.19 x 10^{-7} Scm^{-1}. The frequency dependent conductivity was analysed by Johnscher's power law. Dielectric behavior of the prepared film was studied from the frequency response of dielectric constant (ε′) and dielectric loss (ε′′). Presence of relaxing dipoles was analysed from loss tangent spectrum. The structural changes and complex formation were identified from X-Ray diffraction patterns.

Keywords: polymer electrolyte, ionic conductivity, dielectric properties, XRD

I. INTRODUCTION

Polymer electrolytes fabricated as a flexible film possesses a good electrode-electrolyte contact and form an ideal medium for a wide range of electrochemical processes. This unique feature engage them in practical applications such as primary and secondary batteries, high and low temperature fuel cells, electrochromic devices, modified electrode/sensors, solid-state reference electrode systems, supercapacitors, thermoelectric generators, high-vacuum electrochemistry and electrochemical switching [1]. Therefore, it becomes vital to improve the properties of polymer electrolyte. Ionic conductivity of polymer electrolyte remains a major setback to the development as the value is not equivalent to that of liquid electrolyte. Enhancement in amorphous nature of polymer electrolyte and dissociation of salt with the help of plasticizer, ceramic filler, ionic liquid etc., are the recent techniques followed to improve the ionic conductivity of polymer electrolyte [2]. Moreover, it is important to understand the mechanism of ionic conductivity to improve its property.

The dielectric properties of ion conducting polymer electrolyte provide valuable information on ionic transport behaviour and ionic / molecular interactions in polymer electrolyte. The frequency dependent dielectric properties of polymer electrolytes are very sensitive due to the motion of charged species and polymer dipoles which reveals information on the ion conduction mechanism and its relationship with the dielectric parameters in the system. The variation of relative dielectric constant with frequency indicates that ionic and polymer segmental motion is strongly coupled. The study of dielectric relaxation phenomenon is a powerful tool to understand the mechanism behind ionic conduction.

In the case of P(VdF-HFP) polymer electrolyte, several authors have shown interest to study its thermal, electrical and structural properties [3]. But, to the best of our knowledge, the molecular interactions involving the polar groups of P(VdF-HFP) and the ions of NaTf have not been explored by the earlier investigators. Also, the Na^+ ion hopping responsible for the ionic conductivity has not been analysed so far. These aspects can be brought out through the study of dielectric behaviour of the polymer electrolyte. Hence, it is decided by the authors to study the frequency response of the dielectric constants and the dielectric loss tangent. Also, the Johnscher's universal power law and the jump relaxation model were applied to study the Na^+ ion hopping in the present system.

II. METHODS AND MATERIAL

A. Materials used

Poly(vinylidene fluoride-co-hexafluropropylene) (P(VdF-HFP)) of molecular weight 130,000 $gmol^{-1}$, and sodium triflate (NaTf) were obtained from ALDRICH and used as such. Acetone was purchased from MERCK and used as solvent without further purification.

B. Preparation method

P(VdF-HFP) and NaTf were taken in the ratio 7:3 and dissolved in acetone by mechanical stirring for 8 hrs. The obtained solution was then poured into glass petri-dishe and allowed to dry at room temperature for 5hrs in vacuum. Finally, stable translucent free standing thick film was obtained.

C. Material characterisation

The electrical conductivity measurement of the sample was carried out by AC impedance spectroscopic technique with the help of PSM 1735 impedance analyser. The sample was sandwiched in between two stainless steel electrodes of surface area A and the impedance was measured in the frequency range from 1Hz - 1MHz at room temperature. Thickness of the sample (t) was determined using micrometer screwgauge. AC impedance spectroscopy is used to analyse the dielectric properties of the material. Relative permittivity can be expressed in complex form as in equation (1) given below:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \text{ ---------- } (1)$$

Real part ε' is dielectric constant and the imaginary part ε'' is the dielectric loss. ε'' and ε' can be calculated from the impedance data using the following expressions [4].

$$\varepsilon' = \frac{-Z''}{\omega C_0(Z'^2+Z''^2)} \text{ -------------- } (2)$$

$$\varepsilon'' = \frac{Z'}{\omega C_0(Z'^2+Z''^2)} \text{ -------------- } (3)$$

The ratio between the dielectric loss and the dielectric constant is quantified as tan δ ie,

$$\tan\delta = \frac{\varepsilon'}{\varepsilon''} \text{ -------------- } (4)$$

XRD patterns of the samples were recorded using X'pert PAN analytical diffractometer with Cu-K_α radiation (wavelength, λ = 0.154 nm) for the Bragg angle (2θ) varying in the range from 10° to 80°.

III. RESULTS AND DISCUSSION

A. AC impedance spectroscopy

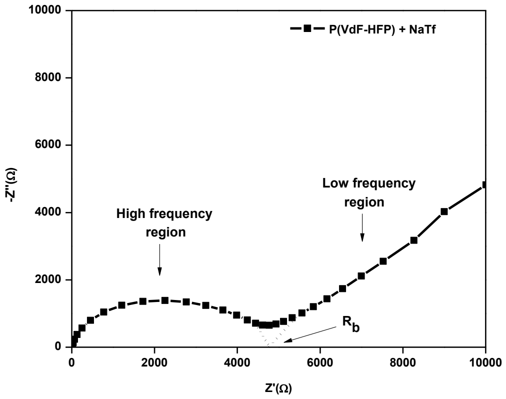


Figure 1 AC impedance plot of P(VdF-HFP) + NaTf

AC impedance plot of P(VdF-HFP) – NaTf, Figure 1, consists of a depressed semicircle arc in the high frequency side and an inclined spike in the low frequency side. In this present work, the semicircle represents the bulk effect of polymer electrolyte which is due to the parallel combination of bulk resistance R_b (ion migration) and bulk capacitance C_b (immobile polymer chain). The depressed semicircle reveals the presence of non-Debye nature of the sample due to the potential well for each site through which ion transport take place. The low frequency spike denotes the effect between two blocking electrodes which represent the formation of double layer capacitance of polymer electrolyte interface produced by the accumulation of ions. Furthermore, the inclination of the spike at an angle less than 90° to the real axis is due to the inhomogeneity at the electrode electrolyte interface [5]. Point of intersection of semicircle on the horizontal axis gives the value of bulk resistance. The obtained value of R_b of the system is used to calculate the ionic conductivity of the sample by the formula $\sigma = \frac{t}{R_b A}$ where t is the thickness of the sample, R_b is the bulk resistance of the sample and A is the area of cross section of the electrode. The calculated value of ionic conductivity is 4.19 x 10^{-7} Scm^{-1}. The interaction between P(VdF-HFP) and NaTf is in such a way that P(VdF-HFP) helps in the dissolution of NaTf by the coordination of Na^+ with F atom of P(VdF-HFP). Due to the non-polar nature of P(VdF-HFP), the coordinated Na^+ easily decouples from the polymer backbone facilitating the transportation of charge carrier and hence leads to the increase in ionic conductivity. The interaction between NaTf and P(VdF-HFP) also reduces the intermolecular interaction among the constituent groups of polymer chains and thus increasing the polymer chain segment flexibility. Enhancement in the concentration of Na^+ charge carriers and improvement in the Na^+ mobility aided by flexible polymer backbone helps to attain ionic conductivity for P(VdF-HFP) – NaTf electrolyte in the order of 10^{-7} Scm^{-1} at room temperature.

B. Frequency Dependent Conductivity

Variation of conductivity with frequency ($\sigma(\omega)$) is investigated to differentiate as well as to identify the origin of the conduction process. The total conductivity $\sigma(\omega)$ can be expressed as the sum of dc and ac components according to the Johnscher's universal power law equation [6]

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac} \text{ ------------- } (5)$$

where σ_{ac} is given by $A\omega^n$ where A is frequency independent temperature related parameter and n is temperature dependent frequency exponent.

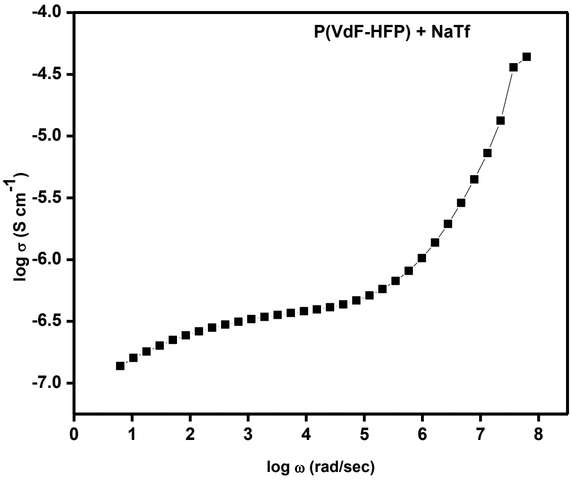


Figure 2. Conductance spectra of P(VdF-HFP) + NaTf

Figure 2 shows the conductance spectra of P(VdF-HFP) + NaTf. Here, the conductance spectrum can be distinguished into three regions – a) low frequency dispersion region, b) mid frequency plateau region and c) high frequency plateau region. Low frequency dispersion region is inferred due to space charge polarisation at the electrode/ electrolyte interface which leads to the accumulation of charges. This is followed by frequency independent plateau region. Extrapolation of this plateau region to zero frequency gives dc conductivity which is consistent with conductivity obtained from Nyquist plot. According to jump relaxation model [7], at this frequency ion jumps from one site to neighbouring favourable vacant site in the host polymer matrix, contributing towards the dc conductivity. As the frequency is increased, the probability for the ion to go back again to its initial site increases due to short time periods leading to forward-backward hopping of ions. This high probability for the correlated forward-backward hopping together with the relaxation of the dynamic cage potential is responsible for the observed high frequency conductivity dispersion.

Using equation (5), the fitting parameters σ_{dc}, A and n are obtained as follows.

Fitting parameters	Value
σ_{dc}	4.15×10^{-8}
A	9.53×10^{-12}
n	0.859

The power law exponent ‘n’ relates the back hop rate to the site relaxation time.

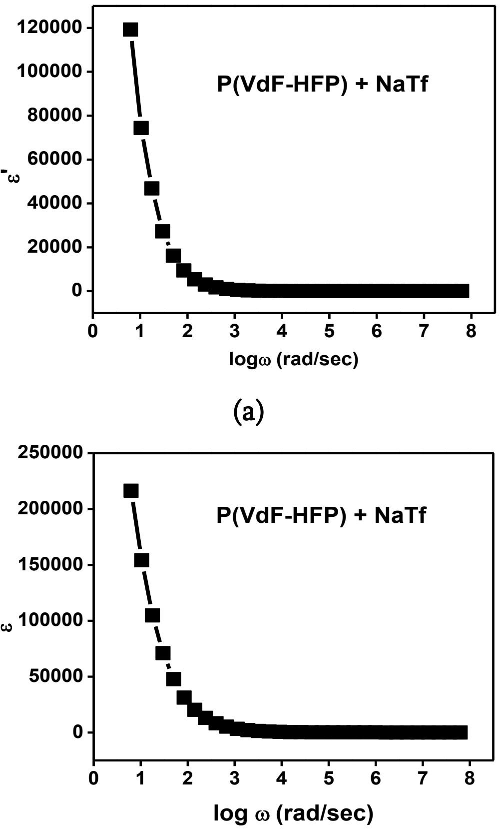
n = back hop rate / site relaxation time

The value on n (0.859) obtained for the sample is less than 1 which implies that the backward hopping is slower than the site relaxation.

C. DIELECTRIC STUDIES

The study of frequency dependence of dielectric constant and its related parameters of polymer electrolyte brings a deep insight into the characteristics of ionic and molecular interactions. It also gives a clear understanding of ion transport mechanism in terms of different relaxation processes in polymer electrolyte.

The frequency dependence of real (ε') and imaginary parts (ε'') of dielectric constant is shown in Figure 3 (a) and (b) respectively. Variation of ε' and ε'' shows similar observation that ε' and ε'' decrease with increase of frequency. A rapid fall of ε' and ε'' at low frequency and their saturation in higher frequency region was observed, which is a typical feature of polymer electrolytes. The short increase of ε' values in the low frequency region is mainly due to the contribution of electrode polarisation (EP) and Maxwell-Wagner(MW) interfacial polarization [8].



(a)

(b)

Figure 3. Frequency dependence of (a) dielectric constant and (b) dielectric loss of P(VdF-HFP) + NaTf system

The EP phenomena in dielectric material occurs due to the formation of electric double layer (EDL) capacitances by the free charges that build up at the interface between the electrolyte and electrode surfaces in plane geometry. The build-up of electrical polarisation and the drop of the electric field in the bulk are reflected in the increase of the dielectric function and decrease of the ac conductivity with decreasing frequency.

With increase of frequency, the fast periodic reversal of the electric field leads to decrease in the long range drift of excess ion diffusion in the direction of the field so that the charge accumulation for the formation of EDL decreases and consequently there is decrease in the ε' and ε'' values. Thus the variation of dielectric constants against frequency confirms the movement of Na^+ ions in the polymer electrolyte

D. Loss Tangent (tan δ)

The study of dielectric relaxation phenomenon using the dielectric loss tangent is a powerful tool to investigate the ion transport behaviour and ionic/molecular interaction in polymer electrolytes. The loss tangent is the ratio of loss factor to the dielectric constant and is a measure of the ratio of electrical energy lost to the energy stored in a periodic field.

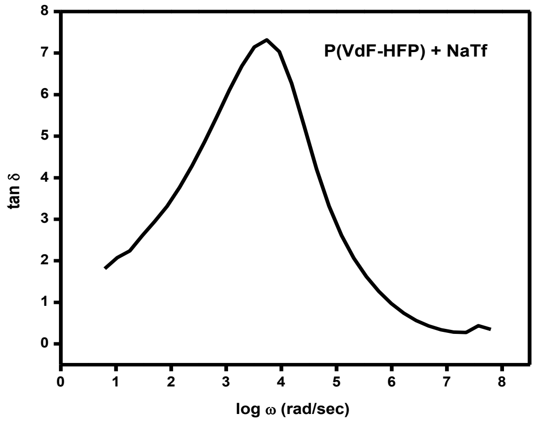


Figure 4. Variation of loss tangent for P(VdF-HFP) + NaTf

The loss tangent spectra of P(VdF-HFP) + NaTf is shown in Figure 4 . The observation of peak in the spectra at particular frequency suggests the presence of relaxing dipoles in the systems. The relaxing phenomenon may be assigned to glass transition of the amorphous component of the polymer [9]. At maximum dielectric loss in the curve, the loss tangent peak is described by the relation, ωτ = 1, where τ is the relaxation time and ω is the angular frequency of the applied electric field. Further, the asymmetry of the peaks is attributed to the merger of more than one relaxation processes and to the non-Debye relaxation behaviour.

E. X-ray diffraction

X-ray diffraction pattern of polymer electrolyte is used to determine crystallinity or to differentiate amorphous, semicrystalline and nanocrystalline states of polymer. The peak positions, intensities, widths and shapes provide important information about the structure of the material which is essential to understand the electrical properties of polymer electrolyte.

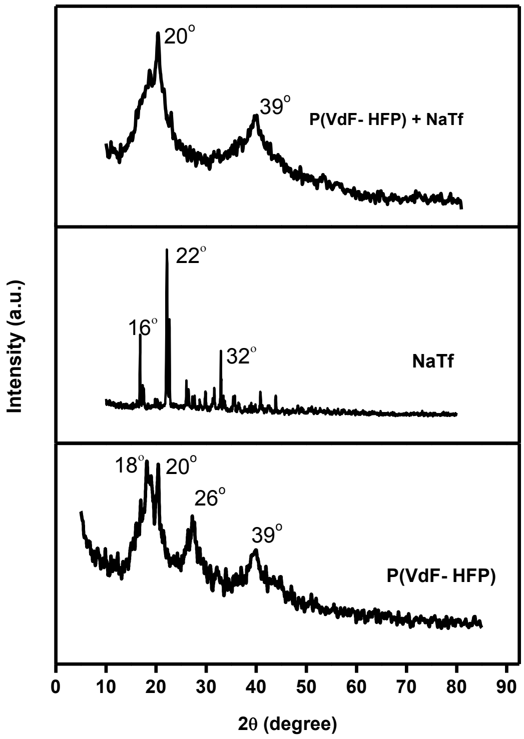


Figure 5. XRD pattern of P(VdF-HFP), NaTf and P(VdF-HFP) + NaTf

Figure 5 shows the XRD patterns of P(VdF-HFP), NaTf and P(VdF-HFP) + NaTf complex. In the XRD pattern of P(VdF-HFP), the characteristic Bragg's peaks appear at the 2θ values 18°, 20°, 26°and 39° corresponding to (100), (020), (110) and (021) planes of crystalline PVdF unit of P(VdF-HFP) [10]. These peaks are seen along with broad hump between 15° and 25° indicating the semicrystalline nature of the copolymer P(VdF-HFP) which possesses the crystalline PVdF and amorphous HFP regions simultaneously [11]. Diffraction peaks at the 2θ values 16°, 22°, 26°, 33°, 40° and 43° of sodium triflate, confirm its crystalline nature.

In the XRD pattern of P(VdF-HFP) –NaTf complex polymer electrolyte, the Bragg's peaks corresponding to P(VdF-HFP), observed at 18° and 26°, were found to be disappeared and peaks at 2θ values 20° and 39° were observed with reduced intensity. This implies that the salt disrupts the crystalline region of P(VdF-HFP) and increases its amorphous nature. In the increasing amorphous domain, the polymer backbones are more flexible which enhances the ionic conductivity [12]. Also, the absence of characteristic peaks of NaTf, demonstrate that complexation has occurred between the sodium salt and the polymer.

IV. CONCLUSION

Polymer electrolyte consisting of poly(vinylidene fluoride-hexafluoropropylene) and sodium triflate was prepared by solvent casting technique by using acetone as solvent. Ionic conductivity of the P(VdF-HFP) –NaTf system was determined as 4.19×10^{-7} Scm^{-1} at room temperature. The dielectric behavior of the prepared samples showed strong dependence on frequency. The variation of dielectric constant and dielectric loss were high for low frequencies and were constant for high frequencies. Appearance of the loss tangent peak at a characteristic frequency suggested the presence of relaxing dipoles. X-ray diffraction studies confirmed the complete dissolution of NaTf in P(VdF-HFP) matrix.

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