



Structural, Ionic Transport and Dielectric Studies of Polyvinyl Formal (PVF) based NCPEs Dispersed with Multiferroic (BFO) Filler

Markandey Singh¹, Kamlesh Pandey² and SL Agrawal³

¹Institute of Technology & Management, GIDA, Gorakhpur, India

²NCEMP, University of Allahabad, Allahabad, India

³Department of Physics, APS University, MP, India

mk.ssi10@gmail.com

ABSTRACT

In the present work, the ion transport property of Polyvinyl Formal (PVF)-based nanocomposite polymer electrolytes has been investigated upon dispersal of Multiferroic (BFO) nanosized filler particles. With the aim to developed the lithium ion (Li⁺) conducting nanocomposite polymer electrolytes (NCPEs) Lithium Acetate has been chosen as doping salt. NCPE films were prepared by solution cast technique while Multiferroic nano powder was synthesized through sol-gel process. The formation of nanocomposite has been ascertained by XRD pattern. Variations of dielectric constant, dielectric loss, tangent loss and modulus spectra with frequency and temperature were studied with the aid of impedance spectroscopy data. XRD result shows that the doping of salt increases amorphousness through polymer salt complexation. The changes in surface morphology have been investigated in optical and SEM images observation. CV measurement of NCPEs suggests a broad electrochemical window utility in practical electrochemical devices.

Keywords: Polyvinyl Formal (PVF), Li⁺ ion conduction, Polymer salt Complexation, Polymer electrolyte, Multiferroic (BFO) filler, Active filler, NCPEs

INTRODUCTION

Recently, Nanocomposite Polymer Electrolytes (NCPEs) materials are receiving highly attention, owing to their potential application in advanced electrochemical devices such as high performance batteries, efficient energy conversion devices-fuel cells, high energy storage- super capacitors, electro-chromic (ECD's) devices, smart windows, actuators etc. [1]. These NCPEs have several advantages over liquid electrolytes such as good mechanical properties, better thermal stability/corrosion less, light weight, high flexibility and ease of fabrication as thin films with suitable size, ability to perform a good electrode-electrolyte contact. Primarily, ionic conduction was only known to exist in liquid electrolytes but after the exhibition of high ionic conductivity in AgI crystals by Faraday [2], a large number of solid ionic conductors were developed and explored to give birth to a new area of science and technology termed as Solid State Ionics. The discovery of ionic conduction in polymers in recent past has provided new dimensions to this fast growing field. Variety of ion conducting polymer electrolytes have been developed over the few years with the aim of achieving highly conducting stable ionic materials for device application purposes. A large number of host polymers [e.g. polyethylene oxide (PEO), Poly methyl methacrylates (PMMA), polypropylene oxide (PPO), polyvinyl alcohol (PVA) and Polyvinyl formal (PVF) etc. have been investigated in the past three decades by complex with a number of alkali, alkaline and transition metal salts (e.g. LiClO₄, LiC₂H₃O₂·2H₂O Mg (ClO₄)₄, LiI, NaI, AgI, AgNO₃, NH₄SCN, NH₄ClO₄, NH₄I etc) possessing strong solvating ability [3].

Recently, particular attention has been devoted to introduce some structural modification in polymer electrolytes in order to increase their electrical performance and improve their thermal, mechanical and electrochemical properties to provide commercial acceptability in different electrochemical devices. Various techniques (like plasticization, copolymerization, etc.) have been adopted to achieve the desired objective of high ionic conduction and better stability in these polymer electrolytes. In this process, another class of polymer electrolyte referred to as 'composite polymer electrolyte (CPE)' has evolved [4]. Polymer electrolytes are usually dispersed with ceramic/inorganic/high molecular weight organic fillers to enhance electrical conductivity and to improve thermal, mechanical and electrochemical stability of the polymer electrolyte films. Such a dispersion of fillers was first suggested by Weston and Steele [5].

Since then, a number of inorganic or ceramic and organic additives have been reported [6]. The advent of nano technology has added new dimension to the subject of composite polymer electrolytes. The downsizing of the third component (filler) has led to emergence of the area of nanocomposite polymer electrolytes (NCPEs) [7].

Further, the invention of nano technology have opened new dimension to the conventional CPEs owing to their large aspect ratio of nano particles with respect to micro particles. The dispersal of nano particles in matrix electrolytes with such large surface areas are expected to not only improves the mechanical properties of electrolytes but also their electrical and electrochemical properties. This has been evidenced in few reported nanocomposite polymer electrolytes recently [8]. These expectations and reported systems have variety of nano filler particles in the development of nanocomposite polymer electrolytes in present work. Since the first report on Al₂O₃ based composite polymer electrolytes by Weston and Steele [5] several oxide materials like TiO₂, ZnO₂, SiO₂, Al₂O₃, CNT, BaTiO₃, ferrites etc[9] have been studied in recent past.

In view of the above, an innovative approach has been made to synthesis and characterizes (PVF-LiC₂H₃O₂.2H₂O-BiFeO₃) NCPE system in present work. Among the different commercially available polymers, Polyvinyl formal (PVF) has been chosen as host matrix for present study, as it has 1-3 glycol & 1-2 glycol structure for ionic conduction and possesses polar characteristics supporting fast ion transport. PVF is formed by addition of formaldehyde and sulfuric acid in PVA leading to its porous structure of PVF-a favorable property for fast ion transport. The structural aspect of composite electrolytes has been studied by XRD and SEM measurement while frequency and temperature dependent behavior of dielectric parameters and a.c. conductivity have been investigated by impedance spectroscopy.

EXPERIMENTAL

Synthesis

Nanocomposite Polymer Electrolyte films (~100-300 μ m thickness) were prepared using solution cast technique. The Polyvinyl Formal (PVF) (Mw. 50,000 ACROS organics) and salt Lithium Acetate (LiC₂H₃O₂.2H₂O) (Rankem, India, AR grade) were used for the synthesis of polymer electrolytes. The sol gel developed Multiferroic (BFO) (BiFeO₃) powder was dispersed stoichiometrically in pristine electrolytes in THF (C₄H₈O, Merck) solvent and stirred for 10-15 hours continuously at ambient temperature. This gelatinous heterogeneous polymeric solution was finally cast in Borosil glasses dish. This solution cast film was dried at 30°C in B.O.D. incubator for controlled evaporation followed by vacuum drying to obtain the solvent free standing films of NCPE. The Multiferroic (BFO) filler powder was synthesized by the standard sol-gel technique. With aim of synthesis of BFO powder the different nitrates (like Bi (NO₃)₃.9H₂O and Fe (NO₃)₃.9H₂O have been used as the starting chemicals. These nitrates were dissolved in double distilled water/ethanol mixture. Tetraethyl Ortho-silicate (TEOS) was taken as precursor material for gel formation. The pH of solution was fixed within 2-3 range. The sol allowed to gel at 50°C. The gel was dried at 150°C for 20 h. Subsequently, this dried gel was subjected to thermal treatment at 700°C (for 2 hours) and 1000°C (for 2 hours) in kenthal high temperature furnace. The dried material was crushed to obtain fine powder of Multiferroic (BiFeO₃)-BFO power with dark red colour.

Characterizations

Structural behaviour of BFO powder and NCPEs films were studied by X-ray diffractometer (Phillips X-Pert model) in the Bragg's angle range (2 θ)=10-70° using Cu-K α radiation (λ =1.542 Å). Optical Micrographs of the films were recorded using computer controlled Leica DMLP polarizing microscope (at magnification 50X). The SEM images of the different composite electrolytes system were recorded with JEOL JXA-8100 EPMA instrument at 15KV. The electrical characterization of the solid polymer composite electrolytes was carried out using impedance spectroscopy on the application of small a.c. signal (~200mV) across the sample cell with Pt-blocking electrodes. The complex impedance parameter was measured with impedance analyser (HIOKI LCR Hi-tester, model 3522, Japan) in the frequency range 40 Hz-100 KHz. Dielectric relaxation behaviours were carried out by the impedance data. Cyclic Voltammeter (CV) measurements of NCPEs were performed on CH-electrochemical workstation model-608D at room temperature making use of two Pt-electrode systems in specially designed sample holder. The cyclic voltammeter has been performed for the 'Pt//NCPEs//Pt' cell with a scan rate 0.1 Volt/Sec. for 10 cycles.

RESULTS AND DISCUSSION

X-ray diffraction pattern of pure PVF and pristine electrolytes are shown in figure-1(a). XRD pattern of pure PVF film casted in THF-DMSO solvent is shown broad peak at ~2 θ =20°. This shows the semi-crystalline nature of pure PVF film. Upon the doping of salt Lithium Acetate (LiC₂H₃O₂.2H₂O) in polymer matrix, decreases the intensity of peak pure PVF and enhancement in broadness of peak area have been observed though XDR investigation. This leads to decrease the crystalline behaviour of PVF. The increases in amorphousness of system were notice through polymer salt complexation. The main reflections from the planes are identified as 24°(012), 33°(104), 40°(202), 49°(024), 53°(112), 62°(208) and 64°(220) confirm to the earlier report on multiferroic BFO [10]. The figure-1(b)

depicts the XDR pattern of BFO powder and NCPEs systems. These XRD planes conforms the formation of Bis-muth Iron Oxide (BFO-BiFeO₃). The average grain size (t_{av}) varies of different composite system are evaluated according to Scherer's Formula [11]

$$t_{av} = 0.94\lambda / \beta \cos \theta \quad (1)$$

where, β is FWHM (Full Width at Half Maxima), θ is the Bragg's angle and λ is the X-ray wavelength.

The average particle size of synthesized BFO powder was calculated by Scherer's formula and has been found t_{av} = 29 nm. After the dispersion of BFO powder in pristine electrolyte system, broadness of electrolyte peak increases which leads to enhancement of amorphous behaviour of electrolytes. This facilitates the fast Li⁺ ion transport in nanocomposite polymer electrolyte system. Thus, from XRD results it can be concluded that Lithium Acetate salt and BFO filler are able to modify in structure host matrix.

The optical micrograph of pure PVF, pristine electrolytes and nanocomposite polymer electrolytes are shown in figure-2. The surface morphology of pure PVF film casted in THF-DMSO shows porous behaviour of host matrix. After doping of salt and BFO powder in pure PVF, heterogeneous surface is seen in optical image of nanocomposite polymer electrolyte [PVF: LiAc: BFO (75:25:01)] system.

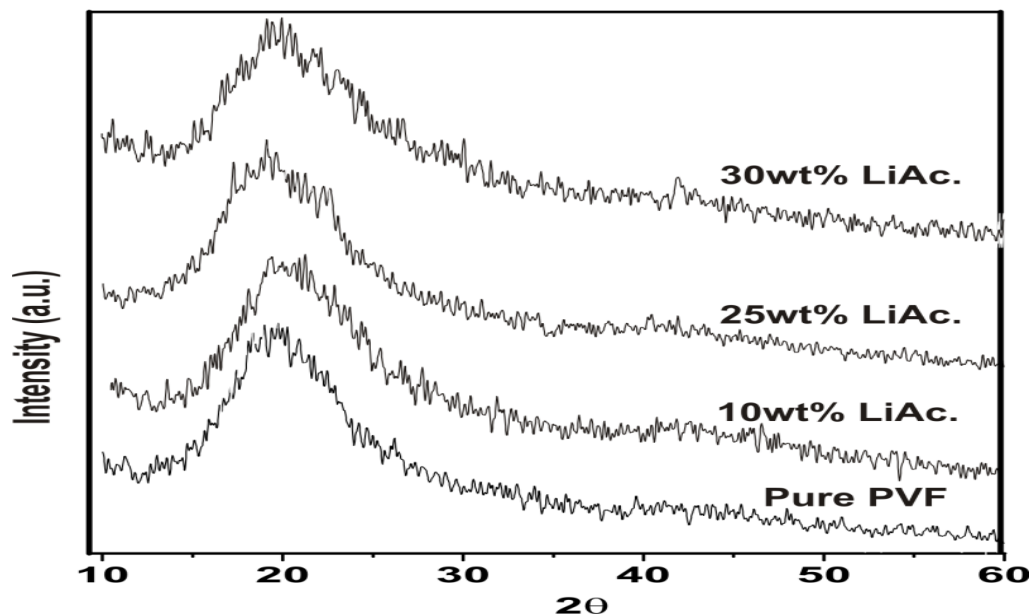


Fig. 1(a) XRD pattern of [(1-x) PVF: xLiAc] polymer electrolyte system, where (x = 0, 10, 25 & 30)

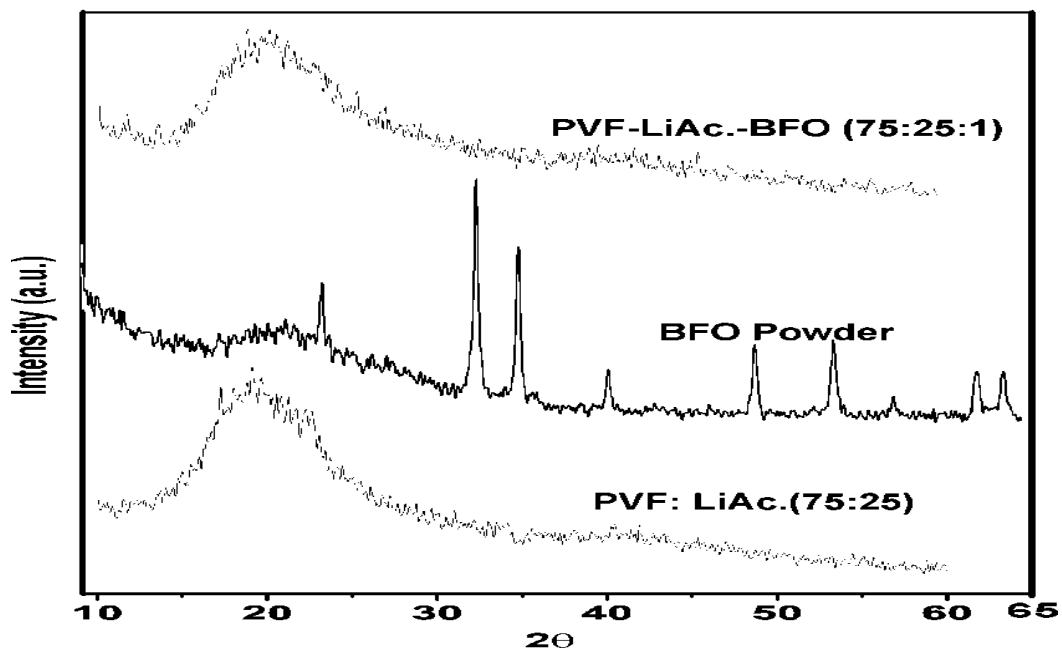


Fig. 1(b) XRD pattern of pure BFO power and PVF: LiAc.: BFO (75:25:1) Nanocomposite Polymer Electrolyte system

Scanning Electron Microscopy of pristine electrolytes, BFO powder and NCPEs are shown in figure-3. After the doping of salt, the cracks in electrolyte films were observed in SEM image which shows solvent swelling characteristics of host polymer. These cracks were observed due to prolonged evaporation of solvent. However, it is observed that surface morphology changes upon the doping of salt as well as changes with increasing salt concentration. At higher salt concentration un-dissolved salt in polymer matrix can be seen in SEM image of PVF: LiAc (75:25) pristine polymer electrolyte. SEM image of BFO powder shows various sizes of BFO particle were heterogeneously distributed. The formation of nanosized format of BFO particles has been estimated during the recording of SEM image at higher magnification. It may see that in PVF: LiAc: BFO (75:25:1) nanocomposite polymer electrolytes BFO nano particles were randomly distributed in polymer electrolyte matrix. However, it can be concluded that salt and BFO filler were compatible for polymer-salt complexation. This confirms formation of nanocomposite polymer electrolyte. BFO powder is able to change the morphology of electrolyte. This is also supports the XRD results of NCPEs.

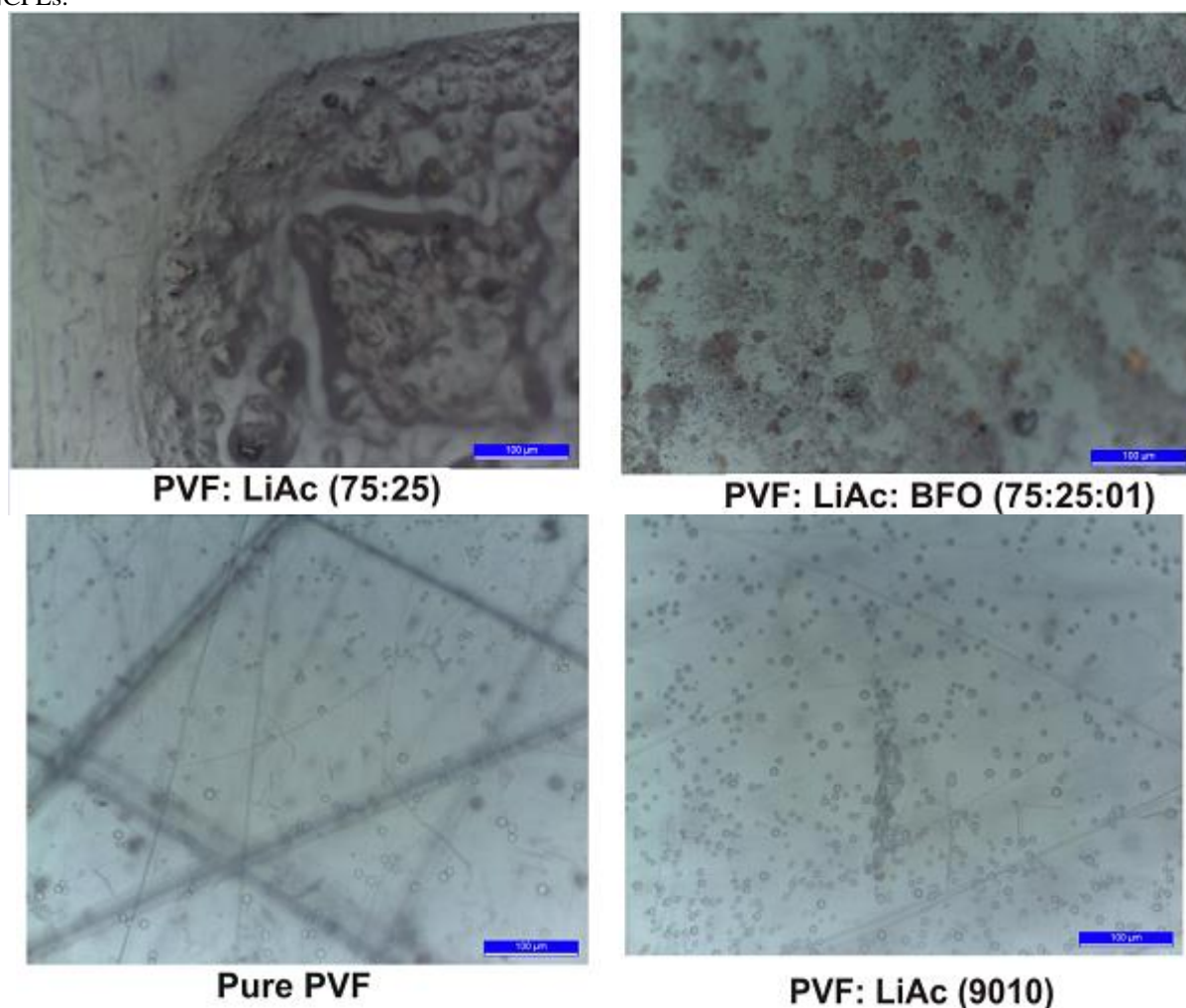


Fig. 2 Optical images of pure PVF, pristine electrolytes, and nanocomposite polyelectrolytes (75:25:1)

The variation of ionic conductivity with concentration of lithium acetate is shown in figure-4 (a). This shows that with the increasing salt concentration the conductivity first increases then starts to decrease up to 15wt% of salt content. Further, the addition of salt in polymer the ionic conductivity again starts to increase and attains maximum value at 25wt% of salt concentration. This type of conductivity behaviour might be correlated to double percolation ionic conductivity model of polymer electrolytes which was earlier reported by Amita Chandra *et al* [12]. The first increase in conductivity may be due to dissociation of lithium salt in the presence of THF-solvent which facilitates the free motion of charge carriers (cation/anion) within the matrix. The decrease in conductivity can be explained with the help of ion association or ion accumulation effect at higher salt content [13-14].

The basic requirements of nanocomposite polymer electrolytes are their ion transporting capability. Knowledge of this capability is therefore pertinent and essential before putting them to use in electrochemical device applications. One of the simplest investigations pertaining to test of ion transporting capability is through polarization behaviour of developed polymer electrolyte systems. Such a study helps researchers to gather information on the nature of species assisting electrical transport and as well as their ability to transfer conductivity species. Thus, the ion transport num-

ber of pristine electrolyte and NCPEs can be evaluated by the Wagner's polarization method [15]. The transport number is measured by the current versus time plot. The variation of current with time is shown in figure-4(b & d). In this plot current initially decreases instantaneously with time. For this measurement design the cell of configuration as Pt/NCPEs/ Pt. Platinum used as blocking electrode and small d.c. potential (200mV) applied for the polarization of our sample for long time period. Under steady state condition migration of cations/ aions due to applied electric field is balanced by diffusion due to concentration gradient.

The transport numbers of ions are calculated by following relation

$$t_{\text{ion}} = \frac{i_{\text{initial}} - i_{\text{final}}}{i_{\text{initial}}} \quad (2)$$

the calculated value t_{ion} of pristine polymer electrolyte has been found above 0.9 which indicate the ionic nature of polymer electrolytes. After the dispersion of BFO powder in pristine electrolyte the small increase in ionic transport number has been notice in PVF: LiAc. BFO (75:25:01) nanocomposite polymer electrolytes. This shows the active role of multiferroic BFO particle which might be involved in ionic conduction though polymer electrolyte. It means multiferroic BFO is active filler.

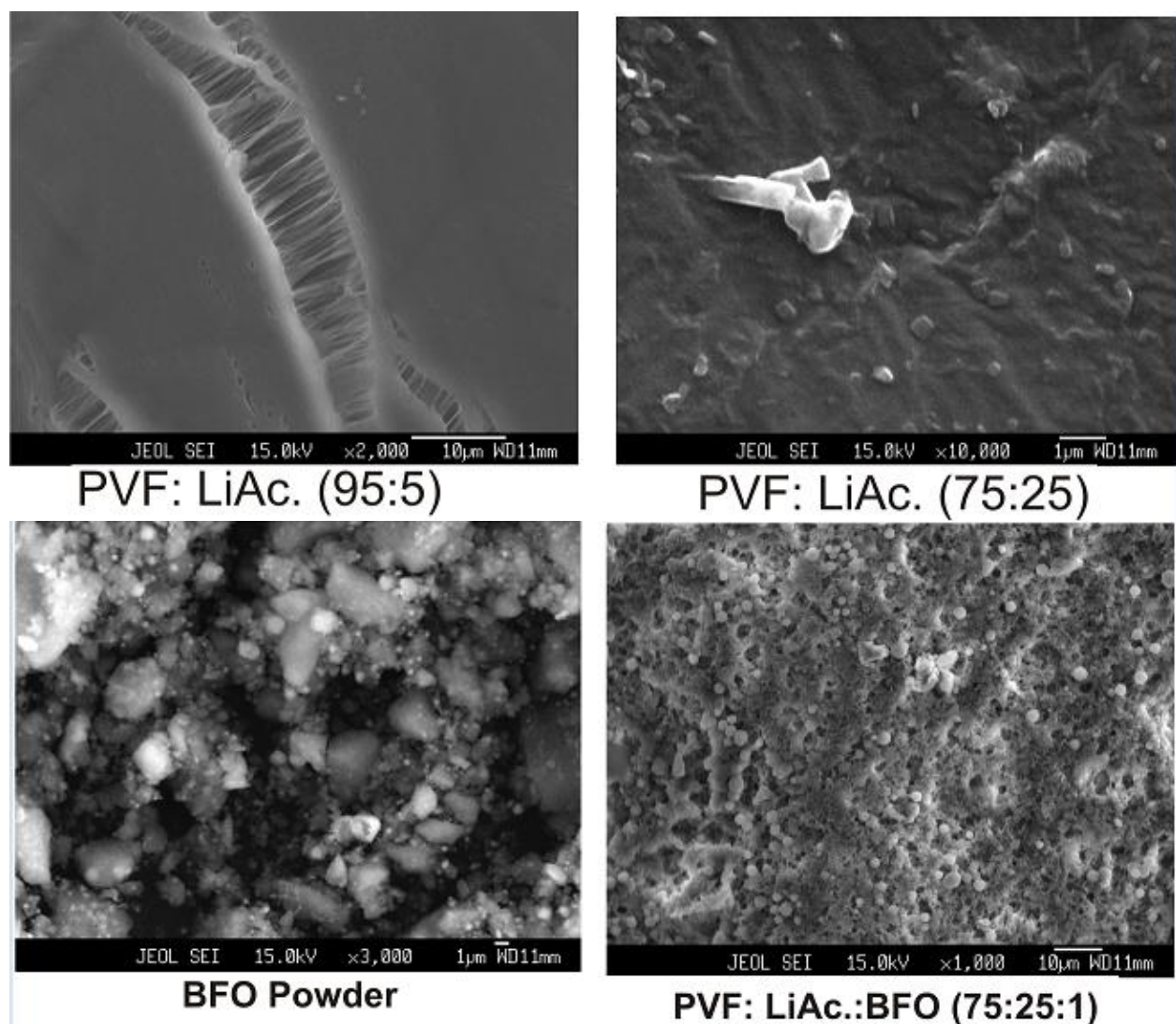


Fig. 3 SEM images of pure BFO power, pristine electrolytes & nanocomposite polymer electrolytes (75:25:1)

NCPEs system. The CV measurement of electrolyte shows good reversibility and electrochemical stability between ± 3 -volt potential. This value suggests the broad electrochemical window utility in practical electrochemical devices. The temperature dependent conductivity of pure PVF and pristine electrolytes is shown in figure-5. The increase in conductivity with temperature is attributed to hopping mechanism between coordinated sites, local structural relaxation and segmental motion of the polymer. As the amorphous region progressively increases, the polymer chain acquires faster internal motion and bond rotations (segmental motions). This in turn favours the hopping of inter-chain

and intra-chain movement and ionic conductivity of polymer electrolyte becomes high. In low temperature region conductivity remains constant followed by temperature dependence behaviour and it increases with increasing temperature. It is correlated to Arrhenius nature separated by a region corresponding to crystalline to amorphous phase transition regime. Thus $\log \sigma$ vs. $1/T$ plot shows a combination of Arrhenius and VTF behaviour described as under

$$\sigma = \sigma_0 \exp(-E_a / KT) \quad (3)$$

and

$$\sigma = \sigma_0 T^{-1/2} \exp(-E_a / T - T_0) \quad (4)$$

where, E_a is the activation energy and K the Boltzmann constant. Low activation energy $E_a = 0.5 \text{ eV}$ of nanocomposite polymer electrolyte suggests their suitability for electrochemical application.

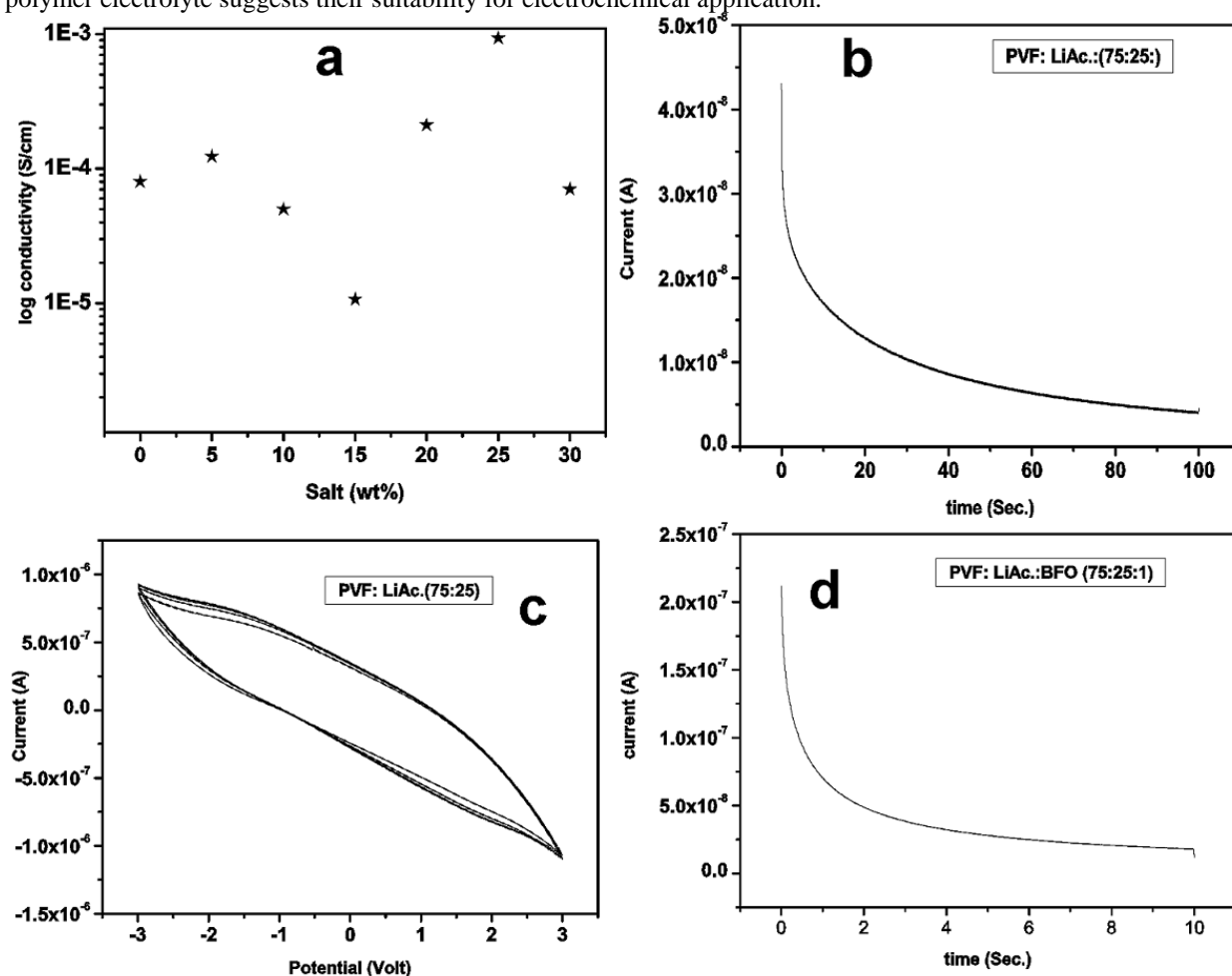


Fig. 4 (a) Variation of ionic conductivity with composition of Lithium Acetate salt (b) Variation of current with time of pristine electrolytes (c) Cyclic voltammetric response of pristine electrolyte (d) Variation of current with time of PVF: LiAc: BFO (75:25:1) nanocomposite polymer electrolyte system

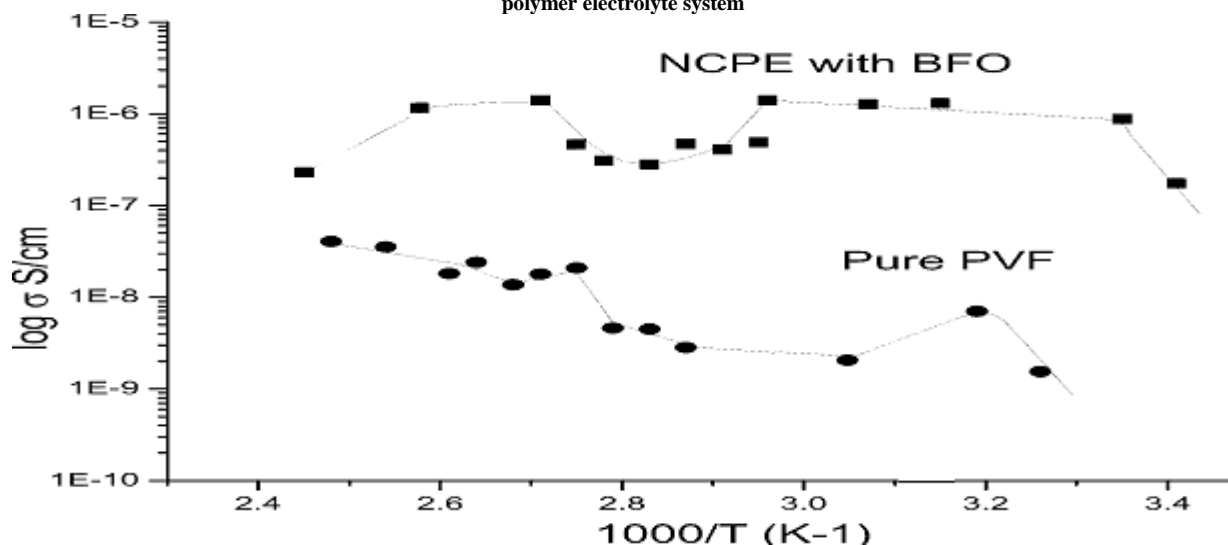


Fig. 5 Variation of ionic conductivity (σ) with temperature of pure PVF & (75:25:1) NCPE

Besides electrical characterization, electrochemical characterization of materials is equally important-especially for electrolytes before using them in electrochemical applications. Cyclic Voltammetry is the most versatile electro-analytical technique for the study of electroactive species, and is widely used in industrial applications and academic research laboratories. Cyclic Voltammeter (CV) is arguably the most widely used technique for the characterization of redox systems [16]. The figure- 4 (c) shows the cyclic voltammetric measurement of PVF: LiAc: BFO (75:25:01)

Figure-6 (a) & (b) shows the variation of dielectric parameters with frequency of [(1-x) PVF: xLiAc] polymer electrolyte system. The permittivity (ϵ' and ϵ'') of electrolyte appears to increase with increasing with salt content, it's also increase being progressively sharp high in low frequency regime. At higher frequency its remains constant and shows frequency invariant behaviour-frequency independent behaviour. This effect might be due to existence of an electrode-electrolyte and interfacial polarization in electrolyte system-The Maxwell-Wagner-Sillars effect [17]. In general, the electrode polarization is attributed to the blocking charge carriers at electrode, which is clarifying the abnormal increase of the real permittivity at low frequencies. On the other hand, an interfacial polarization means the polarization take place at interface of existence of crystalline, absorbed solvent and presence of heterogeneity in NCPs system. The origin of an interfacial polarization is may be also due to trapped solvent in electrolyte matrix, due to the presence of different dielectric media. Another possibilities of the origin of value of ϵ' and ϵ'' in electrolyte system may be traced to the presence of dipolar interaction between Li^+ coordinated to the either oxygen (-O-) of polymer host and anion (CH_3OO^-) present in the polymer electrolyte network.

Figure 6(c) shows the variation of dielectric loss tangent ($\tan \delta$) studies of (1-x) PVF: xLiAc electrolyte as function of frequencies. From this figure it has been observed that $\tan \delta$ increases with increasing salt content. This is due to increase free mobile charge carrier available at higher salt concentration and it follows to decreasing pattern occurred at higher frequency and at still high salt content. This shows the dipole relaxation changing with frequency, is directly a manifestation of polymer chain mobility and its interaction with relaxing dipoles present in the polymer-salt complex. Such a type relaxation phenomena termed as β -relaxation may be attributed to the dipole-polymer segment interaction effect observed normally at room temperature. This peak may be attributed to segmental diffusion motion in amorphous region due to polar groups present in side chain of polymer [14]. The loss occurring due to such interaction depends on a number of factors i.e. the number/ type of constituents in the matrix, the number of repeat units and its mobility, molecular (intra/ inter) interaction and their relaxation time.

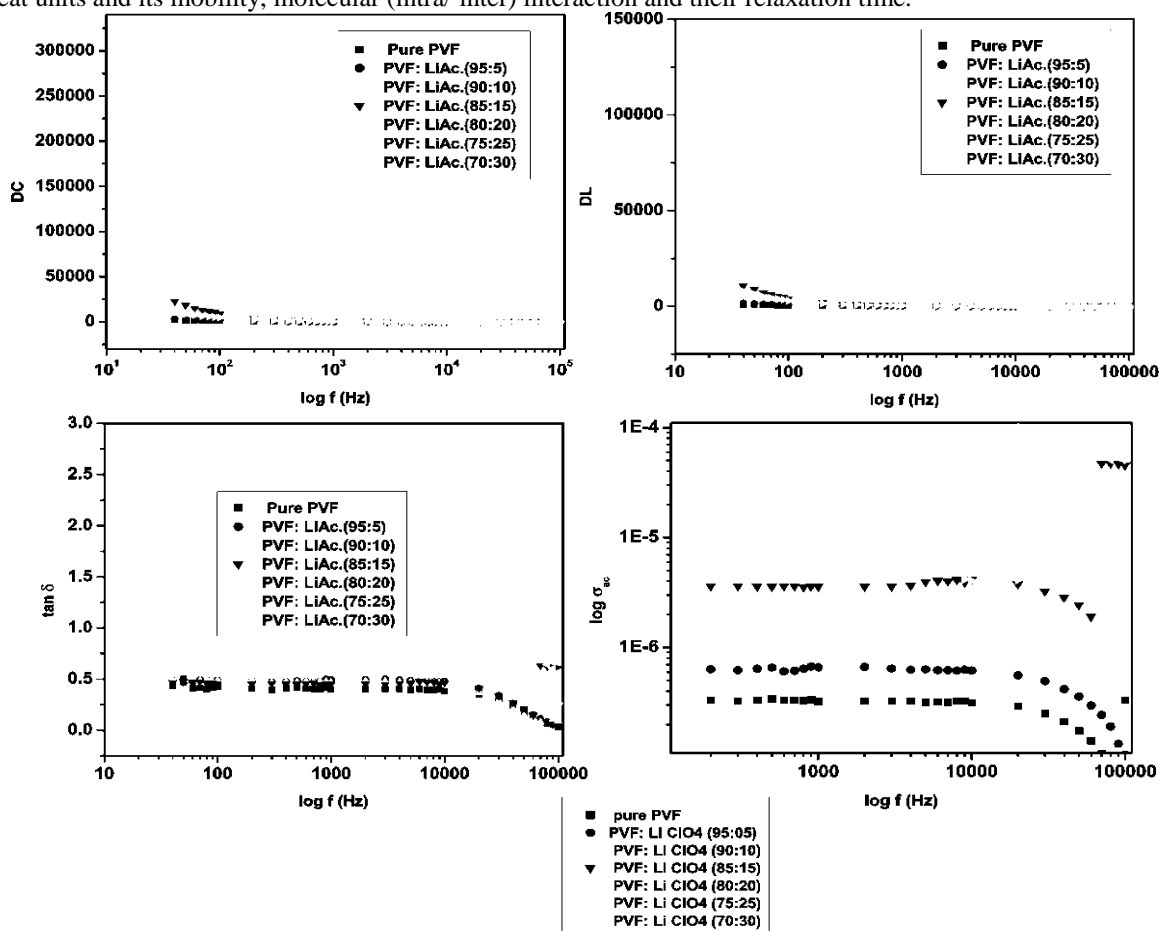


Fig. 6 (a) Variation of (a) real part of dielectric relaxation (b) imaginary part of dielectric relaxation and (c) tangent loss with frequency of pure PVF and pristine polymer electrolyte system

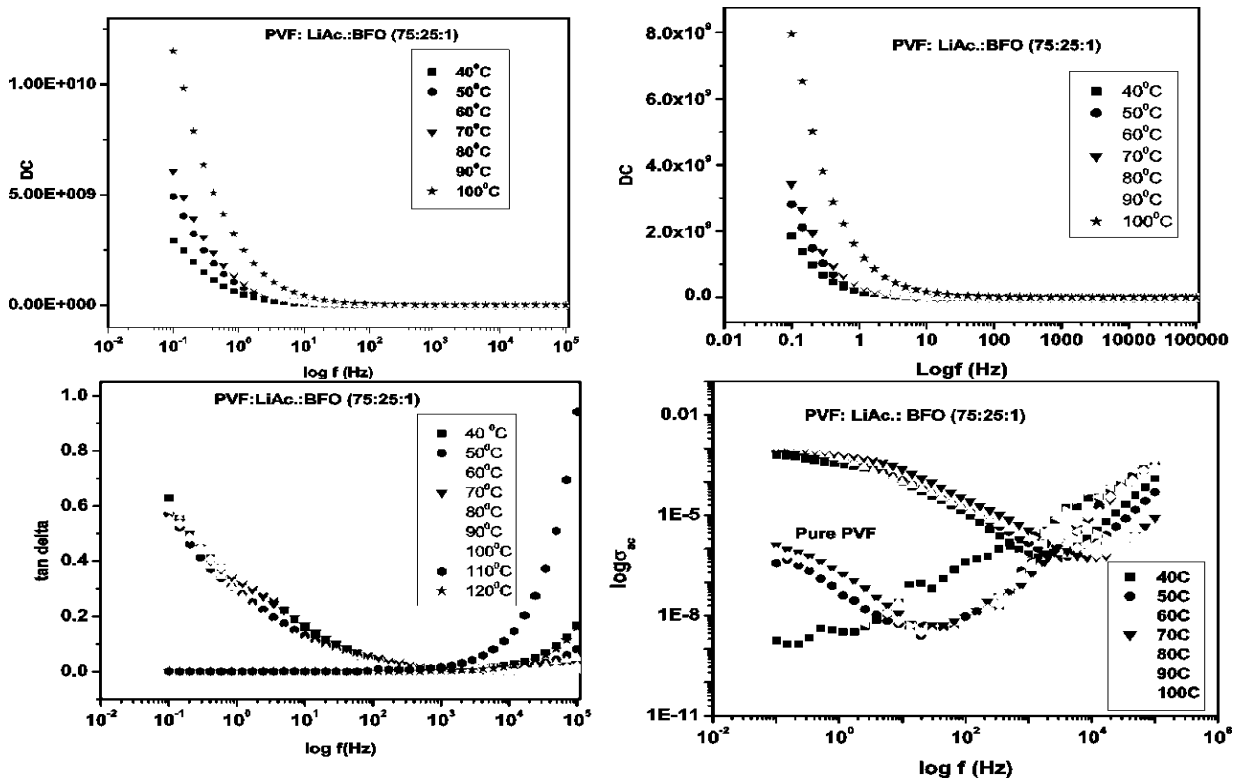


Fig. 7 (a) Variation of (a) real part of dielectric relaxation (b) imaginary part of dielectric relaxation and (c) tangent loss with frequency of PVF: LiAc: BFO (75:25:1) nanocomposite polymer electrolyte system

Figure-7 (a) & (b) shows the variation of dielectric parameters with frequency and at various temperature of (1-x) PVF: xLiAc polymer electrolyte system. The permittivity (ϵ' and ϵ'') of electrolyte appears to increase with increasing with salt content and broad distribution in low frequency regime. At higher frequency its remains constant and shows frequency invariant behaviour [17]. A sharp increase in ϵ' and ϵ'' value with rise in temperature ($> T_m$) may be increased the possibility of the formation of transient dipolar due to ion-ion pair formation in the amorphous electrolyte phase when crystalline to amorphous phase transition ($> T_m$) have occurred. At such higher temperature might be a situation occurred that, polymer matrix becomes more and more flexible with to minimum internal friction leads to permitting faster ion transportation. However, at the higher frequencies, dielectric parameters (ϵ' and ϵ'') factor is low and remains constant with increasing temperature because the orientation of polarization due to chain motion of polymer cannot keep phase the rapidly oscillating applied electric field.

The variation of dielectric loss tangent ($\tan \delta$) studies of PVF: LiAc: BFO (75:25:1) NCPEs electrolyte as function of frequencies at different temperatures polymer electrolytes are shown in figure-7 (c). The tangent loss peak of NCPE system shifted to higher frequency with temperature due fast segmental motion at higher temperature regime. The tangent loss peak in NCPE system is due to the loose segmental packing of chain upon addition of BFO which gives β -transition in amorphous region [7]. A strong interaction among sample constituents is expected to reduce the molecular motion in the matrix resulting in a shift of loss peak towards higher side of the temperature scale. This shift occurs with increasing frequency together with enhancement in the magnitude of loss factor. The β -relaxation is usually detected in the temperature 250-350K and related to with local motion of chain segment or side group.

Figure-6(d) & 7(d) shows the variation of a.c. conductivity of pristine electrolytes and nanocomposite polymer electrolyte with frequency for different temperatures. It is nothing but sum of two parts; one is frequency independent part and second frequency dependent part. The frequency independent of conductivity is called d.c. conductivity and frequency dependent behaviour shows the d.c. conduction in polymer electrolyte. With the increasing salt content, the a.c. conductivity increases which is due to enhancement in charge carrier at higher concentration of salt. This can be easily shown by the Jonscher Power law relation. The frequency dependent conductivity in solid polymer electrolyte system is seen to follow Universal Power law [18].

$$\sigma_{ac} = \sigma_o + A\omega^n \quad (5)$$

where, σ_o is the d.c. conductivity (extrapolation of the frequency dependent region to zero frequency gives the d. c. ionic conductivity), A is the pre-exponential factor and n is the fraction exponent laying between 0 & 1. As the rise the temperature of sample the change in a. c. conductivity is prominently observed with frequency. This means that

the charge carriers are sufficiently free to follow the changing electric field and therefore conductivity frequency dependent. The increase in conductivity at higher temperature might be due to presence of more free ions in NCPE.

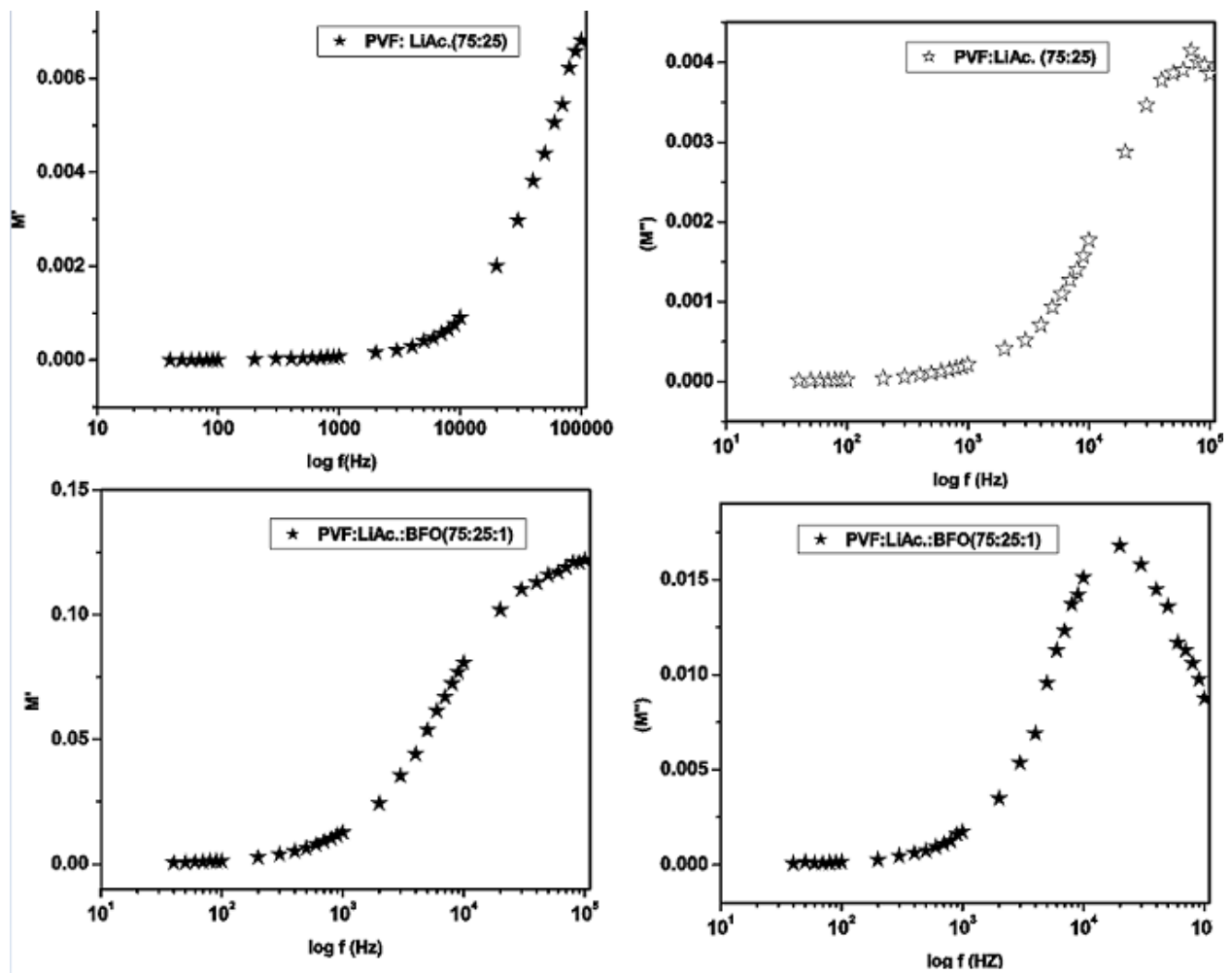


Fig. -8 Variation of real & imaginary part of modulus spectra with frequency of pristine electrolyte and composite polymer electrolyte system

Figure-8(a) & (b) shows the real and imaginary part of electric modulus with frequency of pristine electrolyte and nanocomposite electrolyte system. The imaginary part of electric modulus spectra increases with increasing frequency. In this case, electrode polarization/interfacial polarization effect is seen to completely vanish in contrast to the dielectric formalism.

This is observed around frequencies (<500Hz). The appearance of peak in imaginary part of the dielectric modulus can be assumed to be related with the translation ion dynamics and the conductivity relaxation of the mobile ions. Low values (nearly zero) of M' and M'' in low frequency region is indicative of removal of electrode polarization. Increase of M' with frequency may be due to distribution of relaxation process over the frequency range. This leads the conductivity relaxation spreads over the range of frequency, which gives loss peak in M'' [19-21].

CONCLUSION

Experimental observations of PVF based pristine electrolytes and NCPEs has been focused on the following results. The XRD result shows that Lithium acetate salt is able to change the morphology of pure PVF polymer. Optical image shows porous nature of pure PVF. XRD and SEM observations confirm the Nano crystallite size of BFO powder~29nm. The increase in number of pores in surface morphology has been observed under SEM image investigation. Addition of salt in polymer matrix enhances conductivity up to 2-4 order. Dispersion of BFO powder in electrolyte is able to change the morphology of NCPEs and enhance the ionic conductivity. Multiferroic BFO is involved in ion transport into NCPEs. BFO powder is active filler. CV measurement of NCPEs has shown wide window electrochemical device applicability. Electrode polarization is noticed in DC and DL study at low frequency regime. β -relaxation process is observed in tangent loss studies of NCPE. Modulus study shows removal of electrode polarization at low frequency region. The loss peak in M'' graph is due to electrical relaxation at higher frequency.

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