

## Electrical and Dielectric Behavior of Nano-bio Ceramic Filler Incorporated Polymer Electrolytes for Rechargeable Lithium Batteries

K. Karuppasamy<sup>1</sup>, T. Linda<sup>2</sup>, S. Thanikaikarasan<sup>1</sup>, S. Balakumar<sup>1</sup>, T. Mahalingam<sup>3</sup>,  
P.J. Sebastian<sup>4</sup> and X. Sahaya Shajan<sup>1,\*</sup>

<sup>1</sup>Centre for Scientific and Applied Research, PSN College of Engineering and Technology, Tirunelveli-627 152, India

<sup>2</sup>Marthandam College of Engineering and Technology, Kuttakuzhi, Veeyannoor, Kanyakumari -629 177, Tamil Nadu, India.

<sup>3</sup>Department of Physics, School of Science and Humanities, Karunya University, Coimbatore-641 114, Tamil Nadu, India.

<sup>4</sup>Instituto de Energias Renovables-UNAM, 62580, Temixco, Morelos, Mexico

Received: August 27, 2012, Accepted: January 22, 2013, Available online: April 12, 2013

**Abstract:** A series of nanocomposite solid polymer electrolytes (NCSPE) consisting of PMMA as host polymer, lithium bisoxalato borate (LiBOB) as doping salt and nano-hydroxy apatite as filler have prepared by membrane hot-press method. To enhance the electrochemical properties and stiffness of polymer electrolyte film, a bioactive ceramic filler nano-hydroxy apatite is incorporated in the polymer matrix. The prepared different weight contents of NCSPE films are subjected to various electrochemical characterizations such as ionic conductivity, electric modulus and dielectric spectroscopy studies. The complexation behavior and structural reorganization in polymer electrolytes are confirmed by means of FT-IR (Fourier-Transform Infra Red Spectroscopy) analysis. The electrical response and relaxation of dipole in polymer electrolytes are investigated by means of electric modulus and dielectric studies. The addition of nano-hydroxy apatite significantly enhances the ionic conductivity and blocking the reorganizing tendency of polymer matrix. The maximum ionic conductivity is found to be in the range of  $10^{-4.8}$  S/cm for sample containing 10 wt. % nanoceramic filler.

**Keywords:** nano-hydroxyapatite, PMMA, polymer electrolytes, dielectric studies, ionic conductivity

### 1. INTRODUCTION

The development of electrochemical devices such as batteries, super capacitors, fuel cells and sensors has enhanced rapidly in the past few decades. Vast interest has been shown in the development of rechargeable batteries, especially in gaining a battery that combines long life, environmental safety, compact shape, low cost and high energy density [1, 2]. In order to fabricate better polymer-ion batteries, the electrolyte with good conducting and cycling behavior has essentially required. The polymer electrolyte has drawn great deal of interest due to their wide applications in variety of fields such as rechargeable batteries, fuel cells, sensors, aerospace, automobile and electronic industries. A major drawback in polymer electrolytes that we commonly come across is its low ionic conductivity at ambient temperature. Much attention is focused on

investigating the polymer electrolytes to enhance the ambient temperature conductivity by blending of polymers, cross-linking, and incorporation of inert ceramic fillers [3]. A number of methods are evaluated in order to improve room temperature ionic conductivity. Of these, the widely accepted method is to embed the nano ceramic filler in the polymer matrix. The nanocomposite polymer electrolytes (NCSPE) offer high ionic conductivity at ambient temperatures. In the present investigation, the bio nano ceramic filler can tend to suppress the crystalline nature (amorphous) of polymer thereby increasing the ionic conductivity [4].

PMMA has been used as a polymer host due to its high stability at the lithium electrode-electrolyte surface and because it is less reactive towards the lithium electrode. PMMA is a transparent polymeric material that possesses many desirable properties such as light weight, high light transmittance, chemical resistance, uncolored, resistance to weathering corrosion and good insulating properties. Moreover, MMA (methyl methacrylate) monomer in

\*To whom correspondence should be addressed: Email: shajan89@gmail.com

PMMA has a polar functional group in the main polymer chain that has a high affinity for lithium ions, which are transported. Oxygen atoms from the MMA structure will form a coordinate bond with the lithium ion from doping salts. Hence the increase in effective ionic transport of PMMA based polymer electrolytes may be due to the presence of polar group functional group in PMMA. The bio-ceramic filler nano-hydroxyapatite (NHAp) ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) is chemically similar to the mineral components of bones and hard tissues in mammals and finds applications in membrane separation, dental application, chromatography, gas sensors and high temperature fuel cells [5]. Lithium bisoxalato-borate (LiBOB) is of quite interest due to its high solvating ability, less hygroscopic nature and it yields high ionic conductivity at ambient temperature. Thus, search for the new type of salt is explored. In this regard, LiBOB salt has been identified as the more suitable salt because of its active participation for the formation of SEI and satisfying other basic requisites suggested for polymer electrolytes [6–12]. It contains larger anion which can easily interfere with the crystallization process of PMMA chain, thereby increasing the amorphicity with consequent enhancement of electrical properties. In the present work an attempt has been made to improve and optimize the various electrochemical properties of composite polymer electrolyte by incorporating NHAp to the polymer matrix. In the present work, an attempt has been made to improve and optimize the various electrochemical properties of NCSPE by incorporating NHAp to the polymer matrix. To the best of our knowledge, the vibrational, modulus, and dielectric spectral properties of NCSPE containing NHAp have never been investigated. The details are presented herein.

## 2. EXPERIMENTAL

The precursors, PMMA (Aldrich,  $M_w$   $2.5 \times 10^4$ ), lithium bisoxalato-borate (LiBOB) (Merck) were dried under vacuum for 24 h at 90 °C and 60 °C respectively. NHAp (<100 nm, specific surface area 25 m<sup>2</sup>/g) was purchased from Sigma Aldrich (Germany) and also dried under vacuum at 50 °C for 2 days before use. THF was used as common solvent. NCSPE films of various compositions were prepared by varying the PMMA and NHAp content which was shown in Table (1). The starting materials were dissolved in THF and stirred for about 12 h in order to get a homogeneous mixture. The obtained coagulated pasty mass was allowed to dry in a vacuum oven for 8 h and hot pressed between two stainless steel blocks at a pressure and temperature of 5 tons/cm<sup>2</sup> and 165 °C respectively which finally gave rise to a semitransparent stable NCSPE films of thickness from 100-120 μm. Further the films were dried under vacuum at 80 °C for 2 days for further removal of solvent present in the membrane. Membranes of thickness 100 μm were obtained. Further the membranes were dried under vacuum at 50 °C for 2 days for further removal of solvent present. The result-

ing membranes were visually examined for its dryness and free-standing nature.

### 2.1. Characterizations

Ionic conductivity of PMMA based composite polymer electrolytes have determined by means of electrochemical impedance spectroscopy (EIS) using Zahner IM6 impedance analyzer (Germany). In order to measure the impedance of the films of composite electrolyte, the samples were cut into round shape of 1 cm<sup>2</sup> and fit into size of the electrode. Each electrolyte was sandwiched between two gold plated solid sample holders mounted inside a cylindrical glass container. The experiments were carried out in the temperature range 293 and 423 K. Ionic conductivity measurements were carried out in the frequency range between 100 mHz and 100 kHz with signal amplitude of 1 V. The whole experiments were conducted in a dry moisture free atmosphere. The dielectric and modulus spectroscopic analysis analyses were studied using (Zahner IM6, Germany) electrochemical analyzer for temperatures varying from room temperature to 423 K over wide frequencies range from 100 mHz to 100 kHz. The FTIR spectra were recorded using JASCO FTIR/4100 spectrophotometer (Japan) in the region 400-4000 cm<sup>-1</sup> at room temperature with a signal resolution of 8 cm<sup>-1</sup>.

## 3. RESULTS AND DISCUSSION

### 3.1. Ionic conductivity

The conduction mechanism of NCSPE have examined by means of impedance spectroscopy. The ionic conductivity in polymer electrolyte is assumed to occur by Lewis acid base interaction between salt and polymer solvent [13]. The ionic conductivity depends on overall mobility of ion and polymer which is determined by freevolume around the polymer chain. The ionic conductivity of PMMA-LiBOB based electrolytes are measured for various weight contents of is shown in Table (1). The ionic conductivity of the polymer electrolytes was determined by following equation (1).

$$\sigma = t/(R_b \cdot A) \quad (1)$$

Here,  $t$  and  $A$  were the thickness (cm) and area (cm<sup>2</sup>) of the electrolyte in contact with electrode. Thickness of the film was measured by micrometer screw gauge.  $R_b$  was the bulk resistance (Ω) which was obtained from the nyquist impedance plot. The nyquist impedance plot of sample A3 at various temperatures is shown in Fig. 1(a). It is important to note that at higher frequencies, a compressed semicircle is formed, whereas at low frequencies a spiky line is obtained.

The temperature dependent of ionic conductivity for various PMMA based polymer electrolytes are shown in Fig. 1(b). It is noticed from the figure that, the ionic conductivity increases with increase in temperature. Hence the ionic conduction in polymer electrolytes obeys the VTF (Vogel-Tafmann-Fulcher) relation.

$$\sigma = AT^{-1/2} [e^{-(B/T-T_g)}] \quad (2)$$

Here  $A$  and  $B$  are constants. It can also be noticed that the conductivity increases with increase in NHAp content up to certain wt%. Initially the addition of lithium salt in PMMA matrix leads to formation of PMMA-Li<sup>+</sup> complex. The incorporation of NHAp in the complex form a dative bond with PMMA due to filler-polymer interaction and made easier the migration of lithium ions in the

Table 1. Composition of PMMA, LiBOB and NHAp

Samples	PMMA (Wt%)	LiBOB (Wt%)	NHAp (Wt%)
A1	95	5	----
A2	90	5	5
A3	85	5	10
A4	80	5	15

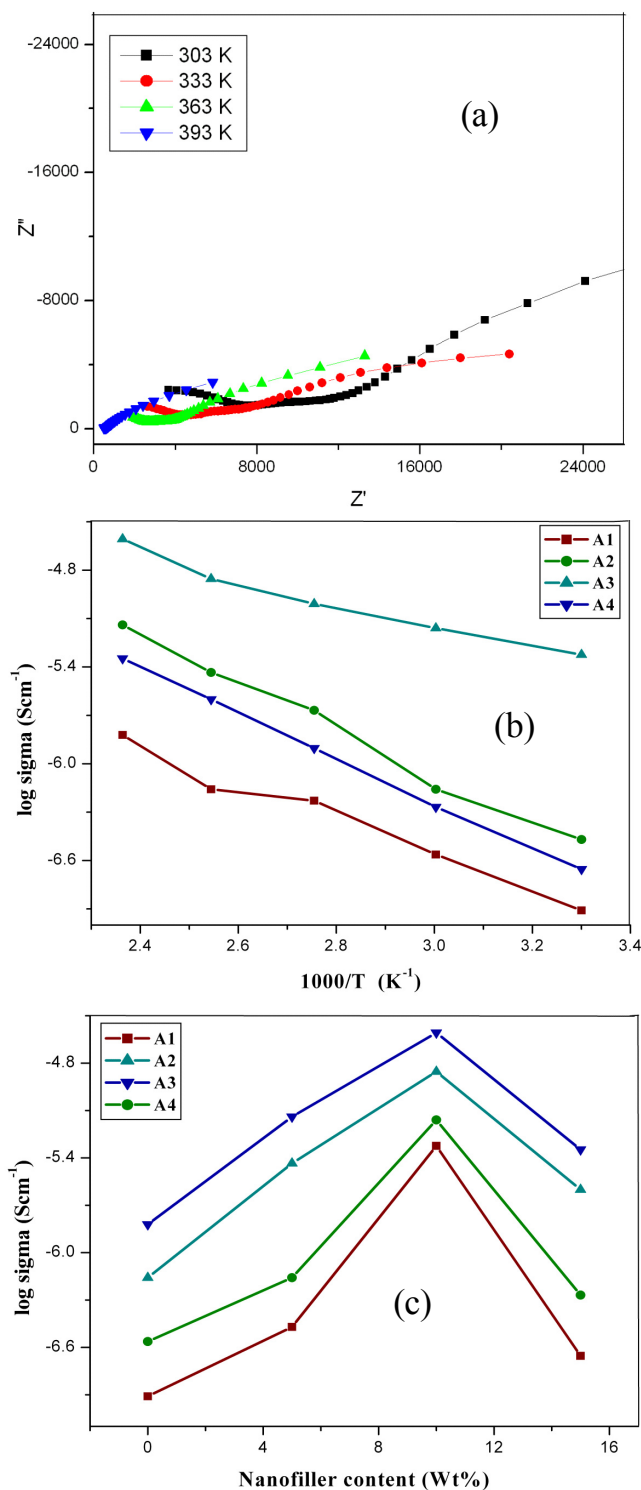


Figure 1. (a): Cole-Cole impedance plot for sample A3 at different temperatures (b): Variation of ionic conductivity as a function of reciprocal of temperature for various nanocomposite solid polymer electrolytes (A1 to A4) (c): The variation of ionic conductivity as a function of nanofiller NHAp content.

PMMA matrix. In the present study, the filler have basic centers can react with Lewis acid centers of polymer chain and leads to reduction in crystalline nature of polymer host. The increase in ionic conductivity with increase in NHAp wt% (up to 10%) may due to the fact that the filler promotes the available number of charge carriers in PMMA matrix by means of creating the free volume around polymer chain. Moreover the PMMA itself contains very small amount of minority carrier where the incorporation of NHAp helps to lower the energy band of the ionic carrier. Hence the ionic transport is faster and easier in the polymer electrolyte by incorporation of NHAp. These results are in accordance with those reported earlier in which  $Al_2O_3$  was used as filler in PEO based electrolyte [15]. In the present work NHAp may act as cross-linking centers for the PMMA segments, which lowers the polymer chain reorganizing tendency and promoting an overall stiffness to the structure. However, the resulting structure provides  $Li^+$  conducting pathways at the filler surface and enhances ionic transport. The maximum ionic conductivity is found to be in the range of  $10^{-4.8}$  S/cm which is two orders of magnitude higher than that of filler free electrolyte A1. Beyond 10 wt% of NHAp, decreases the ionic conductivity gradually due to reassociation of ions into neutral aggregates [14]. This is clearly evident from Fig. 1(c) which shows the effect of NHAp on the ionic conductivity of PMMA based polymer electrolytes. Also the addition of lithium salt (LiBOB) in the polymer is optimized and the optimized wt% is 5. Further increase of LiBOB (not shown in figure) causes the ionic conductivity to decrease gradually due to higher salt concentration; the conductivity decrease may due to the increasing influence of the ion pairs, ion triplets and higher ion aggregation which reduces the overall mobility and degree of freedom [16].

### 3.2. Dielectric analysis

The amount of charge stored in the polymeric material is determined by dielectric permittivity  $\epsilon^*$ . In order to explain the conducting nature of polymer electrolyte, i.e., conductivity is due to available number of free moving ions, dielectric analysis is performed. The complex permittivity of a material can be expressed by means of following expression.

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (3)$$

where  $\epsilon'$  and  $\epsilon''$  are the real and imaginary parts of the complex permittivity and  $j = \sqrt{-1}$ .

The real part of the permittivity is given by:

$$\epsilon' = \epsilon_0 \epsilon_r \quad (4)$$

where  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F/m) and  $\epsilon_r$  is the relative permittivity or dielectric constant of the material [17]. The magnitude of  $\epsilon'$  (or the dielectric constant  $\epsilon_r$ ) indicates the ability of the material to store energy from the applied electric field and the imaginary part of the permittivity,  $\epsilon''$  is called the dielectric loss. Also the capacitance  $C$  is determined by following relation;

$$\epsilon^* = 1 / (jC\omega Z^*) \quad (5)$$

and

$$C = \epsilon_0 A/d \quad (6)$$

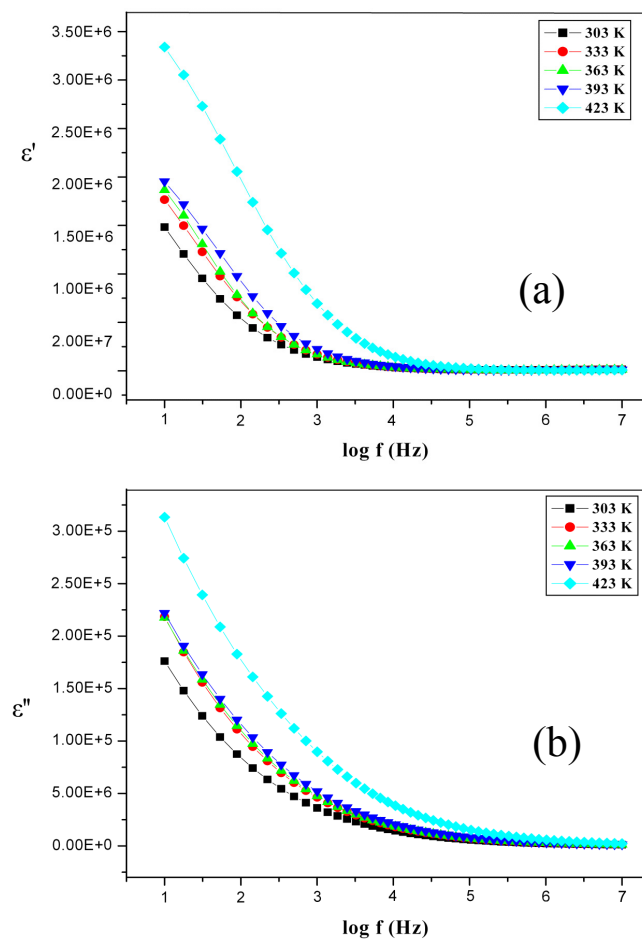


Figure 2. (a) & (b): Frequency dependence of (a) real part  $\epsilon'(\omega)$  and (b) imaginary part  $\epsilon''(\omega)$  of dielectric permittivity for 85% PMMA+ 5% LiBOB+10% NHAp (A3) at different temperatures.

Here  $A$  and  $d$  are area of the electrode and thickness of the electrolyte material respectively.

The purpose of choosing sample A3 is due to the fact that it yields maximum ionic conductivity at ambient temperature. Fig. 2(a & b) shows the variation of  $\epsilon'$  and  $\epsilon''$  as a function of logarithm of frequency. The whole experiment is conducted in the temperature range between 303 and 423 K. At low frequencies both  $\epsilon'$  and  $\epsilon''$  increases gradually due to free charge motion with in the polymeric material. These values do not correspond to the bulk dielectric processes but are due to accumulation of charge carrier density at the electrolyte-electrode interface. At lower frequencies there is considerable amount of time, the charge to build up at the electrode interface. The increase in value of  $\epsilon'$  and  $\epsilon''$  results in increase in equivalent capacitance at low frequency region. The space charge region with frequency is explained in terms of ion diffusion process and generally known as non Debye type of behavior [18]. At high frequencies, the high periodic reversal of applied electric field at the electrode interface takes place, so that there is no excess ion diffusion in the electric field direction. With increasing frequency there was no time for the charges to build up at the interface but

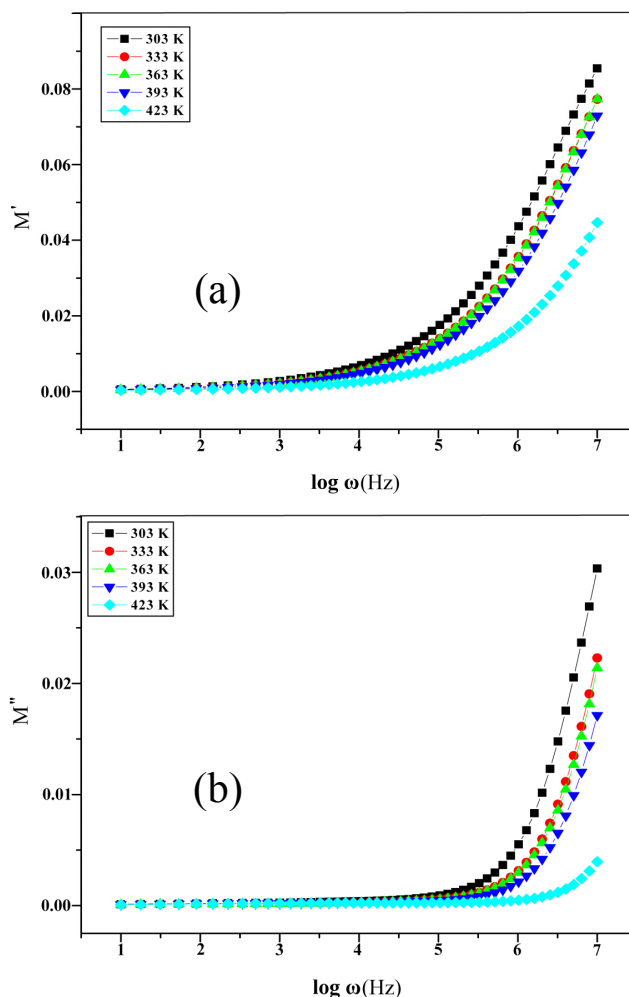


Figure 3. (a) & (b): Frequency dependence of (a) real part  $M'(\omega)$  and (b) imaginary part  $M''(\omega)$  of electric modulus for 85% PMMA+ 5% LiBOB+10% NHAp (A3) at different temperatures.

only to build up at the ends of the conducting paths. Hence polarization due to charge accumulation decreased at the electrode-electrolyte interface. Hence  $\epsilon'$  and  $\epsilon''$  decreases gradually at higher frequencies. The dielectric permittivity ( $\epsilon'$  and  $\epsilon''$ ) increased with temperature which is due to large dissociation of ions occurs at electrode interface.

### 3.3. Electric modulus analysis

The complex modulus  $M^*(\omega)$  is the sum of real part of electric modulus and imaginary part of electric modulus

$$M^*(\omega) = M'(\omega) + jM''(\omega) \quad (7)$$

where

$$M'(\omega) = 1/\epsilon'(\omega) \quad (8)$$

$$M''(\omega) = \omega C_0 Z^*(\omega) \quad (9)$$

Here  $C_0$  is the vacuum capacitance of the cell and  $\epsilon'(\omega)$  is the complex permittivity and  $j=\sqrt{-1}$  respectively. Fig. 3 (a & b) shows the

frequency dependence of  $M'$  and  $M''$  for sample A3 at different temperature. From the figure it is observed that at high frequencies the value of  $M'$  and  $M''$  attains maximum but well defined peaks are not obtained. As the temperature increase, the peaks of  $M'$  and  $M''$  has decreased gradually due to plurality of relaxation mechanism [19, 20]. The value of  $M'$  and  $M''$  tends to be zero in the vicinity at lower frequencies which proposes that the electrode polarization at interface is negligible at lower frequencies. The presence of long straight line in the low frequency region confirms a large equivalent capacitance associated with electrode interface. In the mean time the value of  $M'$  and  $M''$  decreased slowly at higher temperature due to decrease in charge carrier density at the space accumulation region.

### 3.4. FT-IR analysis

The ATR FT-IR spectrum is a powerful tool in order to analyze various functional groups and complexation behavior of polymer electrolytes [21]. The complexation behavior of LiBOB and polymer system with addition of filler could be identified by FT-IR spectra. The FT-IR spectra of pure PMMA, LiBOB, A1, NHAp and A3 are shown in Fig. 4. The characteristic peaks of pure PMMA that appears at 840, 1295, 1394, 1740, 1446 and 2964  $\text{cm}^{-1}$  corresponds to C-O-C bending, C-O stretching, O-CH<sub>3</sub> deformation, C=O stretching, CH<sub>3</sub> bending and CH<sub>3</sub> stretching vibrations respectively which is shown in panel (a). These results are in accordance with the results reported earlier [22]. Also the vibration band that appears at 1372, 1297, 1070, 980 and 604  $\text{cm}^{-1}$  represents B-O stretching, C-O-B-O-C stretching, O-B-O symmetric stretching and B-O deformation vibrational bands of pure LiBOB (panel (b)). The peaks that appears at 3448 and 660  $\text{cm}^{-1}$  in pure PMMA are quite absent during complexation with LiBOB which is indicated in panel (c). Also the vibrational band that appears at 1734  $\text{cm}^{-1}$  of PMMA is substituted by two bands at 1728 and 1731  $\text{cm}^{-1}$  also clearly demonstrate in panel (c). The shifting of peaks in the region from 1144 to 1090  $\text{cm}^{-1}$  indicates that the addition of lithium salt made appropriate change in the polymer matrix. Furthermore, the shifting of peak from 953  $\text{cm}^{-1}$  (pure PMMA) to 951  $\text{cm}^{-1}$  (PMMA+ lithium salt) indicates the complexation behavior of polymer electrolyte. These results strongly confirm the complexation behavior of PMMA with LiBOB. Panel (d) represents the FT-IR spectra of NHAp. The characteristic vibrational band that appears at 3551, 880 and 628  $\text{cm}^{-1}$  are assigned to O-H stretching, CO<sub>3</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> respectively [23]. The incorporation of NHAp in polymer matrix is identified by change in peak positions from 3551 to 3566  $\text{cm}^{-1}$  and 1089 to 1098  $\text{cm}^{-1}$  which is shown in panel (e).

### 4. CONCLUSIONS

Various series of nanocomposite solid polymer electrolytes (NCSPE) comprising of polymer PMMA and LiBOB as salt with different weight ratios of nano bio-ceramic filler hydroxyapatite have been prepared by hot-press method. The effects of NHAp on dielectric and electrical properties of NCSPE have been studied. The maximum ionic conductivity is found to be in the range of 10<sup>-4.8</sup> S/cm for a polymer electrolyte containing 10% NHAp (A3). The low dispersion of  $\epsilon'$  and  $\epsilon''$  revealed that the space charge effects happening from the electrodes. The complexation behavior and interaction between polymer, salt and filler have confirmed by means of ATR FT-IR study.

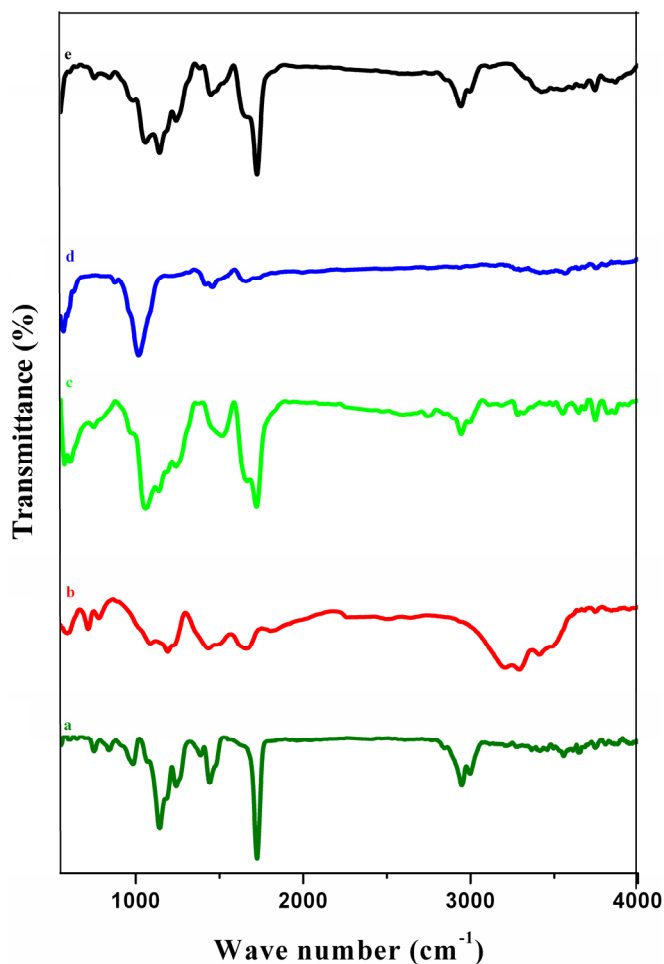


Figure 4. FT-IR spectra of: (a) PMMA (b) LiBOB (S1) (c) PMMA+LiBOB (A1) (d) NHAp and (e) 85% PMMA+ 5% LiBOB+10% NHAp (A3).

### REFERENCES

- [1] F.M. Gray, "Polymer Electrolytes", RSC materials monograph, The Royal Society of Chemistry, Cambridge, 1997.
- [2] J.R. Mc Callum, C.A. Vincent, "Polymer electrolytes Review-P", Elsevier, London, 1987.
- [3] S. Rajendran, M. Sivakumar, R. Subadevi, Mater. Lett., 58, 641 (2004).
- [4] S.P. Low, A. Ahmad, H. Hamzah, M.Y.A. Rahman, J. Solid State Electrochem., 15, 2611 (2011).
- [5] A. Laghizil, N. Elherch, A. Bouhaouss, G. Lorente, T. Coradin, J. Livage, Mater. Res. Bull., 36, 953 (1983).
- [6] W.H. Meyer, Adv. Mater., 10, 439 (1998).
- [7] J.Y. Song, Y.Y. Wang, C.C. Wan, J. Power Sources, 77, 183 (1999).
- [8] B. Scrosati, Chem. Rec., 1, 171 (2003).
- [9] J. Zhou, P. Fedkiw, Solid State Ionics, 166, 275 (2004).

- [10] Z. Florjańczyk, M. Marcinek, W. Wiczonek, N. Langwald, *Polish. J. Chem.*, 78, 1279 (2004).
- [11] A. Manuel Stephan, *Eur. Polym. J.*, 42, 21 (2006).
- [12] A. Manuel Stephan, *Nahm K.S., Polymer*, 47, 5952 (2006).
- [13] A. D'epifanio, F. Serraino Flory, S. Licoccia, E. Traversa, B. Scrosati and F. Croce, *J. Appl. Electrochem.*, 34, 403 (2004).
- [14] W. Wiczonek, Z. Florjanczyk, J.R. Stevens, *Solid State Ionics*, 40, 67 (1996).
- [15] R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T. Hattori, *Mater. Chem. Phys.*, 98, 55 (2006).
- [16] F. Croce, L. Persi, B. Scrosati, F. Serraino-Fiory, E. Plichta, M.A. Hendrickson, *Electrochim. Acta*, 46, 2457 (2001).
- [17] R.D. Armstrong, T. Dickinson and P.M. Wills, *J. Electroanal. Chem.* 53, 389 (1974).
- [18] R.D. Armstrong, T. Dickinson and J. Turner, *J. Electroanal. Chem.*, 44, 157 (1973).
- [19] H.T. Lee, C.S. Lio and S.A. Chen, *Macromol. chem.*, 194, 2433 (1993).
- [20] Dillip K. Pradhan, R.N.P. Choudary, B.K. Samantaray, *eX-PRESS Polym. Lett.*, 2, 630 (2008).
- [21] K. Karuppasamy, S. Thanikaikarasan, R. Antony, S. Balakumar and X. Sahaya Shajan, *Ionics*, DOI: 10.1007/s11581-012-0678-z, 2012.
- [22] H.P. Zhang, P. Zhang, Z.H. Li, M. Sun, Y.P. Wu, H.Q. Wu, *Electrochem. Commun.*, 9, 1700 (2007).
- [23] M.S. Sadjadi, M. Meskinfam and H. Jazdarreh, *Int. J. Nano. Dim.*, 1, 57 (2010).