Effect of Chitin Nanofibres on the Electrochemical and Interfacial Properties of Composite Solid Polymer Electrolytes

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Abstract: *Chitin nanofibres (CNF) are synthesized from a biopolymer chitin by ultra-pure chemical curing method. The nanocomposite solid polymer electrolytes (CSPE) based on PEO-LiBOB with chitin nanofibres as inert nanofiller are prepared by membrane hot-press method. The polymer membrane obtained is subjected to various electrochemical studies such as impedance analysis, cyclic voltammetry and compatibility studies. The crystalline behavior and structural changes in CSPE are investigated by means of XRD and FT-IR analyzes. The filler incorporated membrane shows better electrochemical properties as compared to filler free membrane. The addition of chitin nanofibre in polymer matrix enhances the ionic conductivity and achieves a maximum of $10^{-3.8}$ S/cm. Cyclic voltammetry study is used to know the electrochemical activity of prepared polymer electrolytes at ambient temperature. The compatibility studies reveals that the filler incorporated nanocomposite solid polymer electrolytes reduce the value of interfacial resistance (R_i) and it is better compatible with lithium interface.*

1. INTRODUCTION

Last three decades, solid composite polymer electrolytes (CSPE) arriving a great deal of interest due to their wide potential applications in various fields such as polymer batteries, electrochromic window, fuel cell and sensors [1]. Nowadays, instead of using liquid electrolytes and inorganic crystal in solid state electrochemical devices, the composite solid polymer electrolytes are promising alternatives which possess several advantages such as no internal shorting, good interfacial contact, easy handling and long life time [2-5]. The only difficulty in CSPE that we usually come across is its low ionic conductivity at ambient and sub-ambient temperature. The above said problem is overcome by two ways: (a) addition of low molecular weight plasticizer in the polymer matrix or blending with other suitable polymer (b) to embed nanofiller in the polymer matrix. It is important to note that, the addition of plasticizer or blending with other polymers leads to increase the ionic conductivity but it deteriorates the mechanical stability and strength of polymer electrolytes. In order to improve mechanical stability and ionic conductivity, suitable nanofiller have embedded in the polymer matrix. According to Kumar et al, the incorporation of nanofiller in polymer matrix enhances the polymer segmental motion thereby increases the cation transport number and ionic conductivity at ambient temperature [6].The function of nanofiller in polymer matrix is not only limit to increase ionic conductivity, but also resist the formation of additional passive layer on electrode-electrolyte interface. In the present work, chitin nanofiber (CNF) was employed as filler in polymer matrix.

PEO (poly ethyleneoxide) received much attention as a promising candidate in research of polymer electrolytes for lithium batteries. The nanocomposite solid polymer electrolyte (CSPE) consists of PEO as polymer is more flexible and conforms to any battery shape. It acts as a co-solvent for lithium salt and form stable

polymer-metal complexes via etheral oxygen. Lithium bisoxalato-borate (LiBOB) has identified as more suitable salt because of its less hygroscopic nature and active participation for formation of solid electrolyte interface. The natural linear amino polysaccharide Chitin (N-acetyl-β-D-glucosamine) possesses several interesting properties such as biocompatibility, bioactive, antimicrobial activity, low toxicity and ecological friendly. It finds applications in drug delivery system, paper finishing, solid state batteries, food industries and tissue engineering. Moreover it contains several electron donar groups which can easily interact with inorganic salts. However, to the best of our knowledge, the effect of CNF in PEO-LiBOB complex has never been investigated. The details are presented herein.

2. MATERIALS AND METHODS

LiBOB (Merck), PEO (Sigma Aldrich) were dried under vacuum at 50°C for 48 h before use. Chitin from shrimp shell waste was supplied by Seafresh Chitosan (Lab) Co. Ltd., Thailand. The chitin nanofibre (CNF) was synthesized from shrimp shell chitin after preliminary purification and supplied to us by our collaborator Dr. Paitip Thiravetyan.

2.1. Preparation of nanocomposite solid polymer electrolytes (NCSPE)

CNF was synthesized from chitin as the method described and reported earlier [7, 8]. The synthesized CNF was vacuum dried at 70°C overnight before use. The NCSPE was prepared by membrane hot-press method and details of the preparation method were published by us elsewhere [9]. However, a brief depiction of preparation method is given as follows: The precursor LiBOB was dissolved in various wt% of PEO and stirred for about 4 h. The different wt% of CNF in dimethyl formamide (DMF) was separately stirred for 3 h. The CNF solution was then poured into PEO-LiBOB complex to form the films of PEO-LiBOB-CNF composite polymer electrolyte.The weight ratio of lithium salt to polymer was maintained at 1:8.5 (*w/w*). The above mixed solutions were stirred vigourously for 12 h in order to evaporate solvent. The obtained coagulated pasty mass solution was transferred onto a glass plate and dried under vacuum for 48 h. The obtained film was then cast into membrane by hot-press method. Finally semitransparent free standing film of thickness 100 μm was obtained. The obtained membranes were stored in vacuum desiccators.

3. RESULTS AND DISCUSSIONS

3.1. Ionic conductivity

AC impedance method was used to evaluate the ionic conductivity of NCSPE. The NCSPE's were sandwiched between two gold blocking electrodes of diameter 1 cm and kept in temperature controlled oven in the temperature range from 303-338 K. The thickness (t) and area of cross section of the NCSPE's were 100 μm and 1.0147×10^{-3} m^2 respectively. The ionic conductivity of the NCSPE's was measured using electrochemical impedance analyzer (Zahner IM6, Germany) over the frequency range from 10 Hz-450 kHz with a signal amplitude of 1 V. The reproducibility of impedance spectroscopy results were checked by performing multiple experiments at ambient temperature. The bulk resistance (R$_b$) of NCSPE's were obtained by extrapolation of the semicircular region
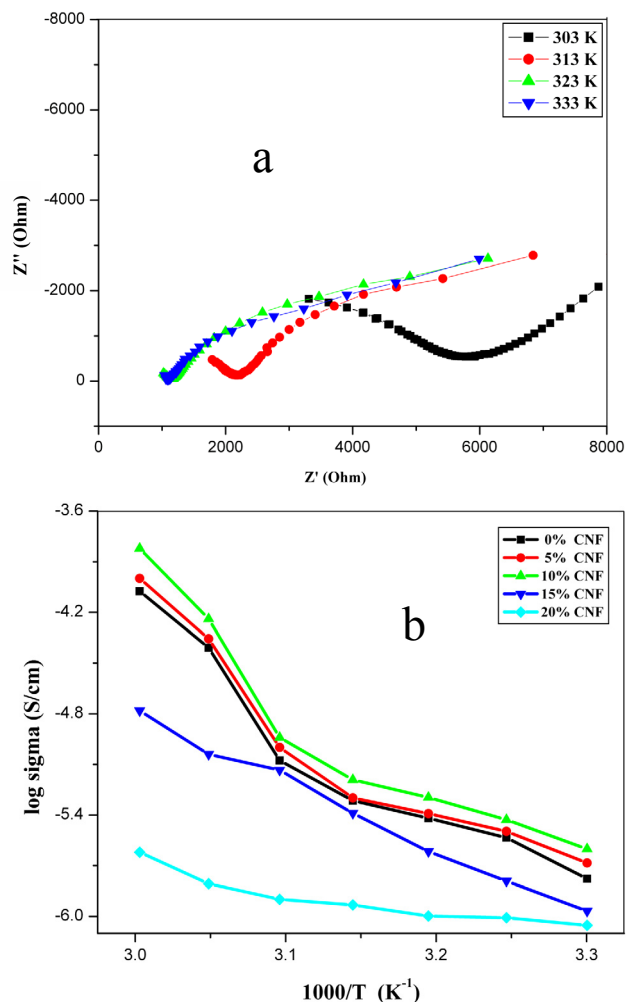

Figure 1. The variation of logarithm of ionic conductivity as a function of reciprocal of temperature for different polymer electrolytes.

to highest frequencies. The cole-cole impedance plot of sample S3at different temperatures are shown in Fig. 1(a). The ionic conductivity (σ) of the prepared NCSPE's was calculated by following equation.

$$\sigma = \frac{t}{R_b A} \tag{1}$$

The variation of logarithm of ionic conductivity as a function of inversion temperature for different wt% of CNF based NCSPE's are depict in Fig. 1(b). As it is evident from the figure that the ionic conductivity of NCSPE's obeys Vogel-Tamman-Fulcher relation [VTF] (eqn.2) i.e., the conductivity increases with increase in temperature.

$$\sigma = \frac{A}{T^{1/2}} e^{-\frac{B}{T - T_g}} \tag{2}$$

where A and B are constants. The constants A and B in VTF

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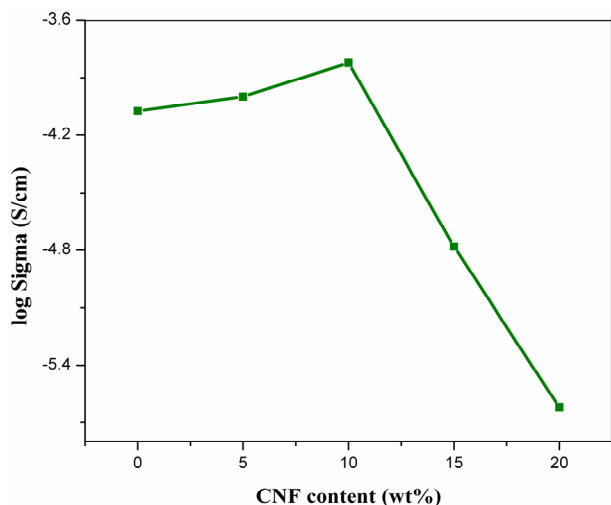
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Figure 2. Variation of ionic conductivity as a function of CNF content for sample S3
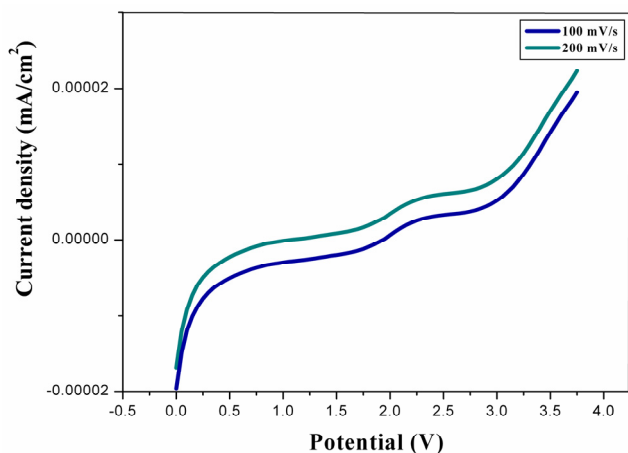

Figure 3. Linear Sweep Voltammogram (LSV) of Sample S3 at different scan rates.

equation are related to number of charge carriers and activation energy of ion transport associated with configurational entropy of polymer respectively [10].

The incorporation of CNF significantly enhances the ionic conductivity of NCSPE's up to 10 wt%. The increase in ionic conductivity is due to the fact that, CNF creates voids or vacancy in the polymer matrix and enhances the effective transport of Li^+ in the polymer matrix, i.e., it acts as a nucleation centre for minute crystallites [11]. Initially the addition of lithium salt in the polymer matrix leads to form PEO-Li^+ complex due to Lewis acid –base type of interactions which was already reported by Wieczoreck et al [12]. After the incorporation of CNF in polymer matrix forms rigid polymer-filler network and enhances the available number of lithium ions thereby increase the ionic conductivity. In the mean time, if the concentration of CNF increases beyond 10 wt%, the conductivity decreases rapidly which is shown is shown in Fig. 2.
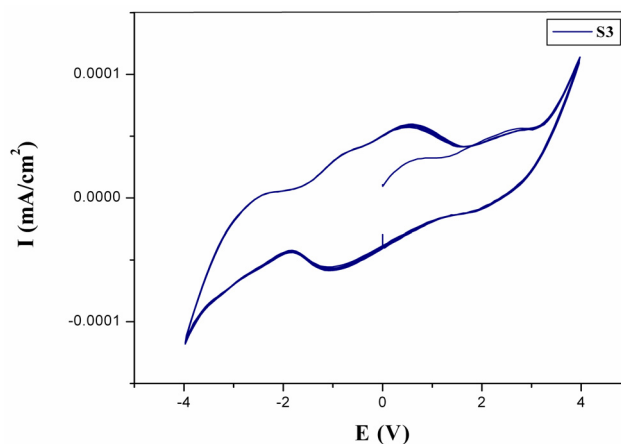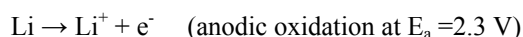

Figure 4. Cyclic voltammogram of sample S3.

This is because of the viscosity of polymer matrix increases by the way of inter-chain self cross linking and results in decrease the polymer segmental motion. Further increasing of CNF content hinders the migration of Li^+ along the polymer chain. Hence the termination of conducting pathway occurs results in decrease the conductivity hastily.

According to Stephan et al.,[13] reported the ionic conductivity of PEO-$LiClO_4$-nanochitin polymer electrolytes was in the range of 10^{-5} S/cm. But in the present work, instead of $LiClO_4$, we have used LiBOB as salt and attained the maximum ionic conductivity of $10^{-3.8}$ S/cm for 10 wt% CNF (S3). In a similar manner, we have optimized the wt% of LiBOB and the optimized level is 5%. Further addition of salt in polymer matrix results in formation of neutral ion pairs as well as decreases the charge carriers in the polymer matrix [14].

3.2. Voltammetry studies
(a) Linear Sweep Voltammetry (LSV) studies

The electrochemical stability of the CSPE has been tested using LSV recorded on SS/CSPE/SS cell. Fig. 3 shows the linear sweep voltammogram of electrolyte sample S3 at two different scan rates. The purpose of choosing sample S3 is due to the fact that it yields maximum ionic conductivity (increases 2 order compared to filler free S1) among all the prepared electrolytes. Both the voltammetric curves shows that the electrochemical window wider than 7 V. It is observed from the figure that, the current I increases slightly with increase in applied voltage V up to certain limit (V_{max}), afterwards it increases suddenly. The CSPE film with CNF as filler displayed the maximum stability window around 3.5 V. The anodic current peak appears at 2.3 V and becomes more pronounced with increasing scan rate of polymer electrolyte. Moreover the curve indicates that one step electro-oxidation occurs and the reaction that takes place at anode is given below.

$$Li \rightarrow Li^+ + e^- \quad \text{(anodic oxidation at } E_a = 2.3 \text{ V)}$$

(b) Cyclic voltammetry (CV) studies

The cyclic voltammogram for cells containing electrolyte sample S3 sandwiched between two symmetrical lithium electrodes are
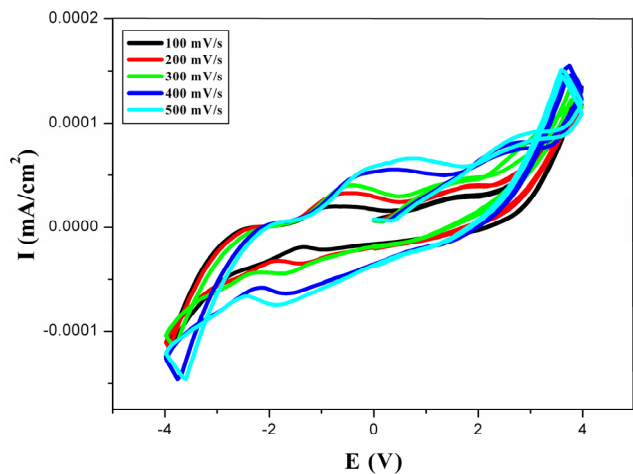
Figure 5. Cyclic voltammogram of sample S3 at various scan rates.

Figure 6. The variation of interfacial resistance R_i with time for polymer electrolytes S1 and S3.

shown in Fig. 4. The sample S3 gives maximum ionic conductivity and possesses better structural and morphological properties. Hence S3 is subjected to CV analysis. The polymer electrolyte S3 shows a well defined redox peak centred at $\Delta E_p = 3.2$ V, i.e., the cathodic and anodic peaks are distinctly observed. The first peak is assigned to oxidation of Li to Li^+. The electro-oxidation reaction occurs only when the potential exceeds 0V.

$$Li + e^- \rightarrow Li^+ \quad (E_a = 0.85 \text{ V})$$

At lower potential the electro-generate Li+ reduces to Li which is assigned as peak 2 in figure and its corresponding electrochemical reaction is given below.

$$Li^+ \rightarrow Li + e^- \quad (E_c = -2.35 \text{ V})$$

The above reversible reaction happens in polymer electrolyte may due to the fact that the formation of rigid filler-polymer network made migration of lithium ion easier in the polymer matrix. Hence the movement of lithium ion is not restricted by filler and polymer. The nanofiller and polymer are electrochemically inactive in the scanned electrochemical window and the electrochemical redox reaction solely depends on the addition of lithium salt in the polymer matrix. Fig. 5 represents the CV pattern for electrolyte S3 at different scan rates. Apart from a small increase in the oxidation and reduction potential, the shape of the waves is unaffected by changing the scan rate. The obtained results are in close agreement with the result reported by Munichandriah et al., [15].

3.3. Interfacial Studies of polymer electrolytes
The specific capacity of lithium (3800 mAhg^{-1}) metal anode is found to be high compared to other carbon based anodes. Hence it is found to be attractive anode material for secondary rechargeable lithium batteries. Various factors affect the cycling behaviour of lithium anode with electrolyte such as (a) reaction of lithium anode with protic and aprotic solvent, (b) electrochemical reaction between electrode and electrolyte and (c) lose of electronic contact between electrolyte and dendritic lithium leads to form resistive passive layer over lithium anode [16]. This results in poor cycling behaviour of polymer electrolyte at electrode interface. Hence the
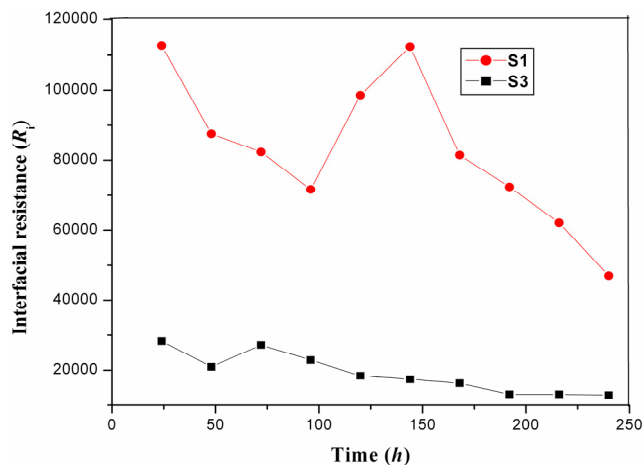
investigation on the interfacial properties of lithium anode with electrolyte is one of the basic criteria for the fabrication of better rechargeable lithium batteries. In the present work, in order to investigate the stability of electrolyte at electrode interface, compatibility studies is carried out by means of constructing symmetric cell Li/NCSPE/Li containing electrolytes S1 and S3 . The whole experiments were performed in an inert N$_2$ atmosphere at 60 °C for 240 h continuously. The purpose of choosing electrolyte S3 is due to the reason that it yields maximum ionic conductivity at ambient temperature.

The variation of interfacial resistance R_i with time for symmetric cells containing S1 and S3 are shown in Fig. 6. It is observed from the figure that the electrolyte S3 is found to be more suitable when lithium metal as anode because the value of interfacial resistance R_i has been reduced by the incorporation of CNF as compared to filler free electrolyte S1. Moreover the value of Ri does not follow a uniform manner. i.e., it decreases slowly with time and then increases. The sudden increase in R_i at 72 h may due to reaction of lithium metal anode with polymer electrolyte. Afterwards it decreases gradually. This may be due to the reason that the morphology of passivated film changes with time to finally acquire a non compact porous structure.

3.4. X-ray diffraction analysis
The XRD pattern of pure PEO, S1 and S3 are shown in Fig. 7 panels (a-c). The XRD pattern for synthesized CNF is already reported [8]. In panel a, the peaks that appeared at an angle $2\theta = 19.51°$ and $23.73°$ corresponds to crystalline PEO. The XRD pattern for S1 in panel (b) is quite similar to that of pure PEO due to the fact that the added lithium salts are completely dissolved in the polymer matrix. Panel (c) represents the XRD pattern of NCSPE S3. The peaks at an angle $2\theta = 22.5°$, $25°$, $17.9°$ and $29.4°$ corresponds to 101, 130, 110 and 202 reflection planes of CNF. The incorporation of CNF in the polymer matrix results in diminishes the peak intensity and the peak becomes broadened. This is due to the fact that there is reduction in crystalline nature of polymer by implantation of filler. Hence the incorporation of high filler content (wt %) enhance the amorphous region, thereby in-
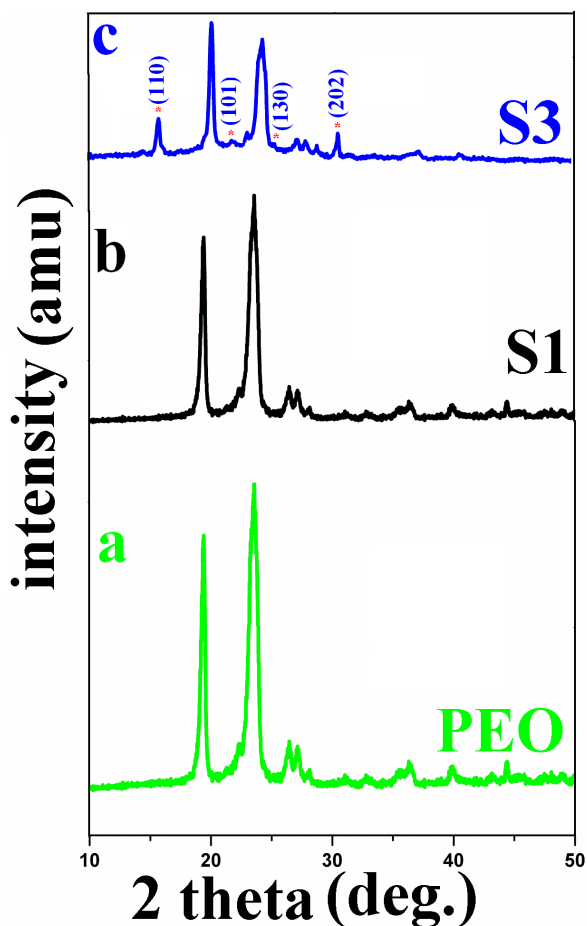
Figure 7. XRD pattern of (a) PEO, (b) S1 and (c) S3.

Figure 8. (a & b): Scanning Electron Micrograph images of S1 and S3.

creases the ionic conductivity.

3.5. Scanning Electron Microscopy (SEM) analysis of NCSPE

The SEM image of polymer electrolytes S1 (filler free) and S3 (filler incorporated) are shown in Fig. 8 (a & b). The SEM image of S1 looks like rock's surface and the surface is extremely hard. The SEM image of S3 reveals that the incorporation of CNF content is the responsible for the cause of uniformly interconnected wrinkle wave structure on the surface of the electrolyte. The presence of wrinkle wave on the surface may due to interaction of rigid filler-polymer network.

3.6. FT-IR analysis

FT-IR analyses were carried out using Jasco FT-IR/4100 (Japan) spectrophotometer in the wave number range from 4000-400 cm^{-1} with a signal resolution of 4 cm^{-1} at room temperature. The whole experiments were recorded in transmittance mode. The FT-IR spectra of pure PEO, LiBOB, S1, CNF and S3 are shown in Fig. 9 (panel a-e). The characteristic vibrational bands that observed at 2880, 1961, 1476, 956 and 841 cm^{-1} corresponds to C-H$_{str}$, asymmetric CH$_{2\,str}$, CH$_2$ scissoring, C-O-C$_{str}$ and CH$_2$ wagging modes of
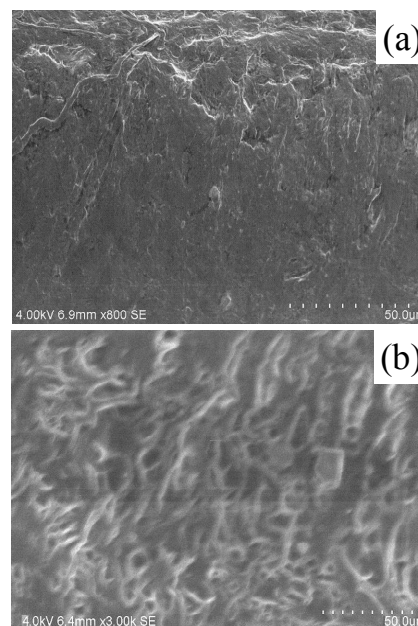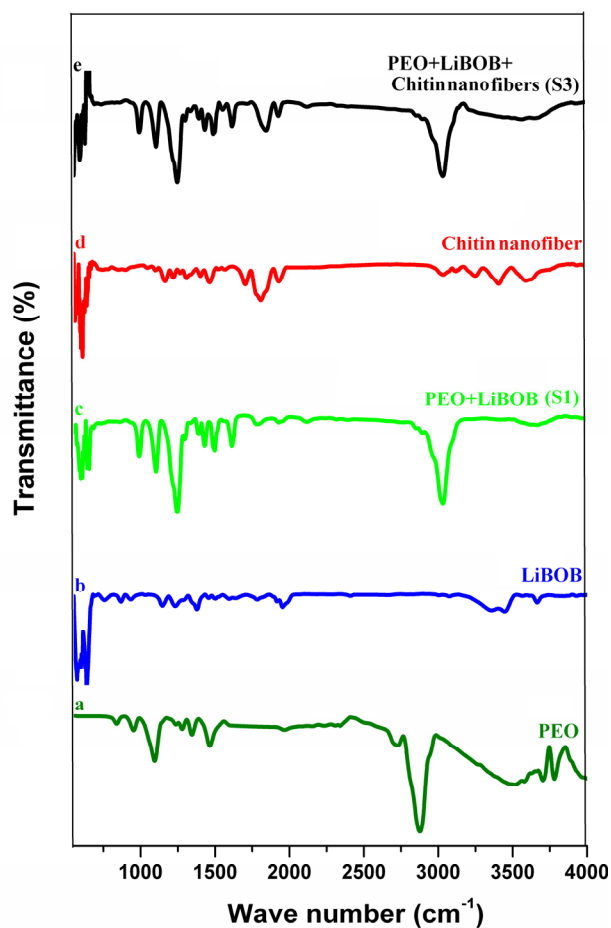

Figure 9. FT-IR spectra of (a) PEO (b) LiBOB (c) S1 (d) CNF and (e) S3.

pure PEO. In figure panel (b) corresponds to LiBOB. The peaks that appeared at 604, 982, 998 and 1301 cm^{-1} are assigned to B-O deformation, O-B-O symmetric stretching and C-O-B-O-C stretching vibrations of LiBOB. The complexation behaviour of lithium salt with PEO can identified by the shifting of peaks from 2880, 1103, 958 and 604 cm^{-1} to 2978, 1099, 960 and 608 cm^{-1} which is shown in panel c. The synthesized CNF vibrational peaks are demonstrated in panel (d). The characteristic peak that appeared at 3740, 2888, 1732, 1582, 1340 and 880 cm^{-1} has assigned to O-H stretching, C-H stretching, N-H stretching, C=O hydrogen bonded to N-H of neighbourhood inter sheet chain and polysaccharide group. The implantation of CNF causes some appropriate changes in polymer matrix. The shifting of peaks from 2880, 1732, 1582 and 880 cm^{-1} to 2885, 1728, 1594 and 884 cm^{-1} which is shown in figure 9 panel (e). Thus FT-IR spectra play a predominant role for the structural investigations of polymer electrolytes.

4. CONCLUSIONS

In the present investigation, various weight content of CNF incorporated NCSPE's were prepared by membrane hot-press method. The ionic conductivity of nanocomposite polymer electrolytes was increased on increasing the experimental temperature and attained a maximum of 10$^{-3.8}$ S/cm. The complexation and structural reorganization of CSPE was analyzed by XRD and FT-IR studies. The electrochemical stability of the polymer membranes were investigated by linear sweep voltammetry and cyclic voltammetry techniques. Moreover the prepared membranes possessed uniform surface morphology due to addition of filler and compatibility study suggested that the filler/plasticizer implanted electrolyte S3 possessed better interfacial resistance (R_i) value than filler/plasticizer free electrolyte S1.

5. ACKNOWLEDGEMENTS

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-I", Elsevier, London, 1987.

[3] A.M. Stephan, Eur. Polym. J., 42, 21 (2006).

[4] T. Uma, T. Mahalingam, U. Stimming, Mater. Chem. Phys., 90, 245 (2005).

[5] J. Adebahr, N. Byrne, M. Forsyth, D.R. MacFarlane, P. Jacobsson, Electrochim. Acta, 48, 2099 (2003).

[6] B. Kumar, L.g. Scanlon, J. Power Sources, 52, 261 (1994).

[7] K. Gopalan Nair, A. Dufresene, Biomacromol., 4, 1835 (2003).

[8] Rujira Dolphen, Paitip Thiravetyan, Chem. Eng. J., 166, 890 (2011).

[9] K. Karuppasamy, S. Thanikaikarasan, R. Antony, S. Balaku-mar, X. Sahaya Shajan, Ionics, DOI: 10.1007/s11581-012-0678-z.

[10] M. Sukeshini, A. Nishimoto, M. Watanabe, Solid State Ionics, 86, 385 (1996).

[11] W. Wieczoreck, Z. Florjanczyk, JR. Stevens, Solid State Ionics, 40, 67 (1996).

[12] W. Wieczoreck, J. Przyuski, Solid State Ionics, 36, 136 (1989).

[13] A. Manuel Stephan, T. Premkumar, M. Anbu Kulandainathan, N. Angulakshmi, J. Phy. Chem. B, 113, 1963 (2009).

[14] Mohd Rafie Johan, Leo Bey Fen, Ionics, 16, 335 (2010).

[15] Munichandraiah Nookala, Binod Kumar, Stanley Rodrigues, J. Power Sources,111, 165 (2002).

[16] A. Manuel Stephan, K.S. Nahm, T. Premkumar, M. Anbu Kulandhainathan, G. Ravi, J. Wilson, J. Power Sources, 159, 1316 (2006).