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Short Communication

Effect of $LiBF_4$ Salt Concentration on the Properties of Poly(Ethylene Oxide)-Based Composite Polymer Electrolyte

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Composite polymer electrolytes (CPEs) comprising a poly(ethylene oxide) (PEO) and nickel oxide (NiO) with different concentrations of lithium tetrafluoroborate ($LiBF_4$) are prepared using a solution casting technique. The structure and complexation of the electrolytes are studied by X-ray diffraction (XRD). The ionic conductivities of the electrolytes are measured at room temperature and shown that the addition of salt weight percent increased the ionic conductivity. The maximum conductivity (8.75×10^{-4} Scm^{-1}) is obtained for a polymer complex with 30 wt. % $LiBF_4$. Scanning electron microscopy analysis showed that a rough surface of morphology of CPEs became smoother with addition of salt.

Keywords: Polymer electrolytes; Ionic conductivity; Poly(ethylene oxide); Nickel oxide

1. INTRODUCTION

In recent years, polymer based solid electrolytes are of major technologies important due to their application in various electrochemical devices such as high energy density batteries, fuel cells, sensors, supercapacitors, smart windows and display devices [1]. The studies on these existing polymer electrolytes are based mostly on PEO and its copolymers because of their strong solvating ability with a variety of monovalent, divalent and transition metal salts [2]. Particular attention has been focused on the study of PEO based polymer electrolytes complexed with lithium and sodium salts because of their direct application in high energy density rechargeable batteries. This conventional ion-conducting polymer has, in general, multi-phase nature, pure PEO spherulite crystalline phase and an amorphous phase with dissolved salt. It has been revealed that the ion conduction takes place primarily in the amorphous phase and the phase diagram is affected by many factors, such as the salt species, preparation method, concentration, temperature and thermal history. Several modifications in the structure of these polymer electrolytes have been realized in order to enhance their electrical conductivity and to improve their thermal, mechanical and electrochemical properties. Alternatively, the addition of inorganic filler, namely, ceramic filler to the polymer electrolytes has recently become an attractive approach due to the mechanical stability and enhanced ionic conductivity and to electrolyte-electrode interface stability. The dispersion of inorganic fillers in polymer electrolytes to improve their mechanical strength was first suggested by Weston and Steele [3]. It has been well established that the addition of inorganic fillers improved the conductivity of polymer host and their interfacial properties in contact with the lithium electrode. Since then, a number of inorganic fillers have been reported in literature, such as α-Al_2O_3, $LiAlO_2$ [4], and SiC [5]. Lithium salts like $LiClO_4$ and $LiBF_4$ are being used as charge carriers in the polymer electrolytes because of Lewis acid behaviour which can interact with electron donor centres. The smaller size of Li^+ could contribute to ion dissociation resultant from coulombic interaction forces between the two oppositely charged ions [6].

In this work, PEO-NiO(10 wt. %) as a polymer host-filler is doped with various wt. % $LiBF_4$ to form composite polymer electrolyte by solution casting technique. These polymer electrolytes were characterized by using electrical impedance spectroscopy (EIS), x-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. MATERIALS AND METHODS

2.1. Reagents and electrolyte film preparation

The starting materials are PEO (M_w 600,000, Sigma-Aldrich, St. Louis, MO), $LiBF_4$ (Fluka/Sigma-Aldrich, St. Louis, MO), NiO powder with mean particle size of about 100 nm was produced by a sol-gel method from $Ni(NO_3)_2$ (Sigma-Aldrich, St. Louis, MO) and tetrahydofuran (THF; SYSTERM; ChemAR, Kielce, Poland). To prepare the polymer electrolyte film, 2.7 g of PEO were dissolved in THF and were continuously stirred with a magnetic bar for 24 h at 55^{o}C. This solution was stirred for 24 hours to obtain a homogenous solution. 10 wt. % NiO were dissolved separately in THF and mixed with the mixed solution and stirred efficiently for 24 h to achieve a homogenous mixture. Then, $LiBF_4$ were dissolved separately in THF and pour into the mixed solution and further stirred for another 12 hours before the casting process. The solution was cast on a teflon mould and allowed to evaporate completely at room temperature. Residual solvents were further removed in vacuum oven for 24 h at 50^{o}C. The samples were stored in a desiccator until further use. The same experimental procedure was repeated for different weight percent of $LiBF_4$.

2.2. Sample characterization

The ionic conductivity measurements were carried out by EIS using High Frequency Resonance Analyzer (HFRA) model Solartron 1255, Sclumberger and electrochemical interface (SI 1286) with applied frequency from 1 MHz to 100 Hz at 30 mV amplitude. The disc shaped sample of 16 mm in diameter was sandwiched between two stainless steel block electrodes. XRD model D-5000 Siemens was used to observe the appearance and disappearance of crystalline or amorphous phase as a function of salt content. The data was collected from the range of diffraction angle 2θ from 10° to 50° at scan rate 0.04° s^{-1}. Surface morphology of sample was observed by using SEM model LEO 1450VP ZEISS with 1200 magnification at 20 kV electron beam. Sample was fractured in liquid nitrogen and coated with gold sputtered-coated machine before the analysis. Analysis was done at room temperature.

3. RESULTS AND DISCUSSION

3.1. Ionic conductivity

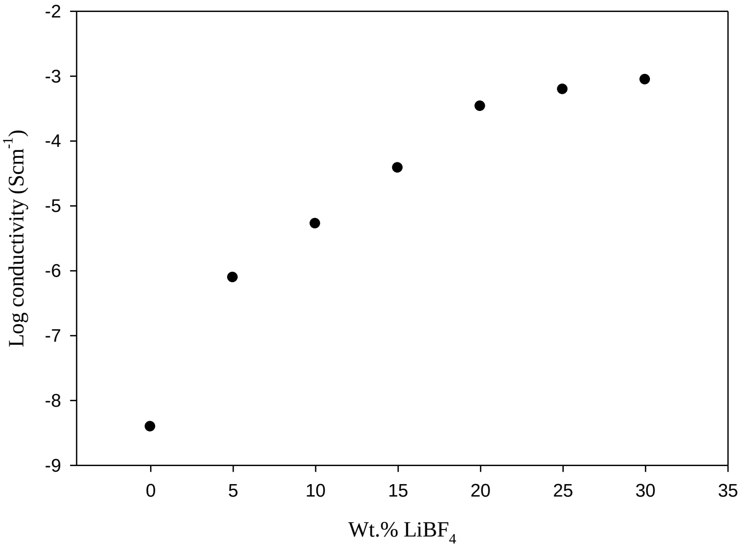

Figure 1. Variation of ionic conductivity of PEO-NiO-$LiBF_4$ electrolyte with different wt. % of $LiBF_4$

The ionic conductivity is a crucial property to be considered to produce a better polymer electrolyte. The resulting conductivity is represented by overall mobility of ion and polymer determined by the free volume which leads to the increase in ionic and segmental mobility that will assist ion transport and practically compensates the retarding effect of the ion clouds [7]. The conduction process in this electrolyte system is due to the hopping of positive or negative charges from lithium salt doped in the polymer host. The ionic conductivity values (σ) of the electrolytes are calculated by using Equation 1, where l, A are the thickness and known area of the electrolyte film ($A = \pi r^2 = \pi\ (0.80\ cm^2)^2 = 2.01\ cm^2$) and R_b is the bulk resistance of the electrolyte film which obtained from the intercept of real part of complex impedance plot. Ionic conductivity of PEO-NiO-$LiBF_4$ electrolytes with variation of wt. % $LiBF_4$ was presented in Fig. 1.

$$\sigma = \frac{l}{A \cdot R_b} \qquad \text{Equation (1)}$$

It shows that the ionic conductivity increases as the salt content increases up to its optimum level in the polymer host. Ionic conductivity without salt content (0 wt. % salt) is 3.91×10^{-9} S cm^{-1}. The optimum conductivity was obtained at 30 wt. % of $LiBF_4$ with the ionic conductivity of 8.75×10^{-4} S cm^{-1}. This work produced a higher conductivity than the finding reported in [8]. The optimum conductivity is probably due to the effective interaction between the charge carriers and the polymer, which influences the segmental mobility of the polymer chains [9,10]. At higher salt concentration, the mean distance between ions becomes more significant because the ions become closer to one another and tend to associate.

3.2. Structural studies

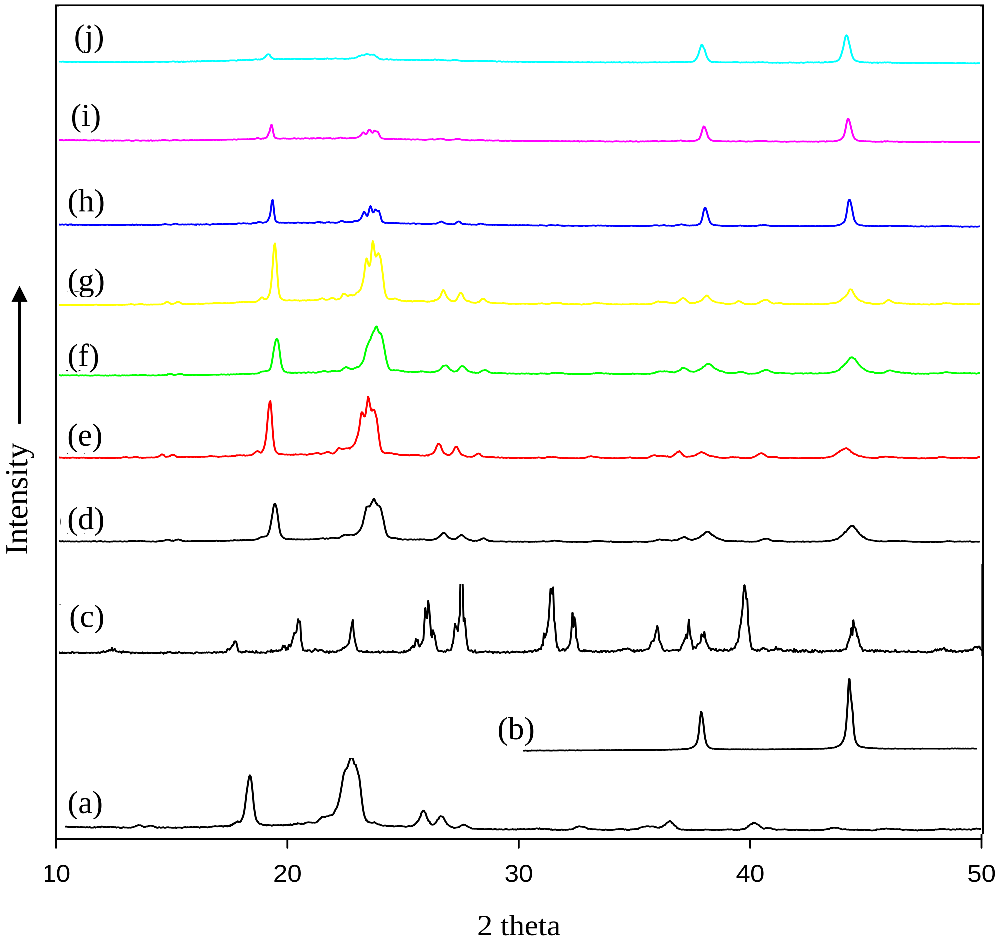

Figure 2. X-ray diffraction patterns of (a) PEO, (b) NiO, (c) $LiBF_4$, (d) PEO-NiO(10), (e-j) PEO-NiO-$LiBF_4$ with various $LiBF_4$ content

The appearance of amorphous region or the reduction of crystalline region would give a high ionic conductivity as compared to the crystalline or semi-crystalline region as reported elsewhere [7,9, 11,12,13,14]. The x-ray diffraction patterns of $LiBF_4$ salt, PEO, NiO, PEO-NiO and PEO-NiO-$LiBF_4$ complexes are presented in Fig. 2. $LiBF_4$ salt peaks are observed at the diffraction angle of 14^o, 21^o, 23^o, 26^o, 28^o, 32^o, 39^o, and 44^o.

The intense peak shows the crystalline region occurs in the polymer host and the amorphous region occurs when the intensity of the peak become broader [15]. As mentioned before, the highest ionic conductivity was obtained at 30 wt. % $LiBF_4$. From the XRD patterns shown in Fig. 2, the highest ionic conductivity are located at 30 wt. % of $LiBF_4$ salt loading which have broadening intensity. In other word, amorphous region appears in polymer host. This finding confirmed the suggestion by [11,12,16,17] that amorphous region possesses high ionic conductivity compared to the crystalline region. The salt affects the overall conductivity through crystalline complex formation, intramolecular cross-linking of the polymer chains and degree of salts dissociation-number of charge carriers [11].

3.3. Morphology Studies

Morphology studies were carried out by SEM to investigate the effect of $LiBF_4$ salts content on the surface morphology of the PEO-NiO composite polymer electrolyte. SEM micrographs of various CPEs are presented in Fig. 3. The micrographs were taken from the fracture surfaces of samples. Fig. 3(a) is the surface image of pure PEO film. The image shows a rough morphology with a great deal of micro-pores, a common occurrence for PEO-based electrolytes prepared by the solvent casting method. It shows the presence of crystalline phase in PEO [18]. A dramatic improvement of surface morphology from rough to smooth is achieved Fig. 3(b) after the addition of Li salt. The smooth surface morphology is closely related to the reduction of PEO crystallinity via the interaction between PEO segments and lithium cations.

The reduction of PEO crystallinity arises from random distribution and dissociation of salt which may introduce the topological disorder in the electrolyte. The reduction of crystallinity will produce more amorphous phase in the system which makes the electrolyte more flexible, resulting in increase of the segmental motion of the polymer [19]. The incorporation and high dispersion of $LiBF_4$ in PEO-NiO complex further improves the surface morphology as evident in Fig. 3(d-e). According to the previous reports [20,21,22], the conducting ions move more freely in the electrolyte with smoother surface morphology and therefore cause the enhancement in the conductivity. This is because smoother surface with more amorphous phase makes the electrolyte more flexible.

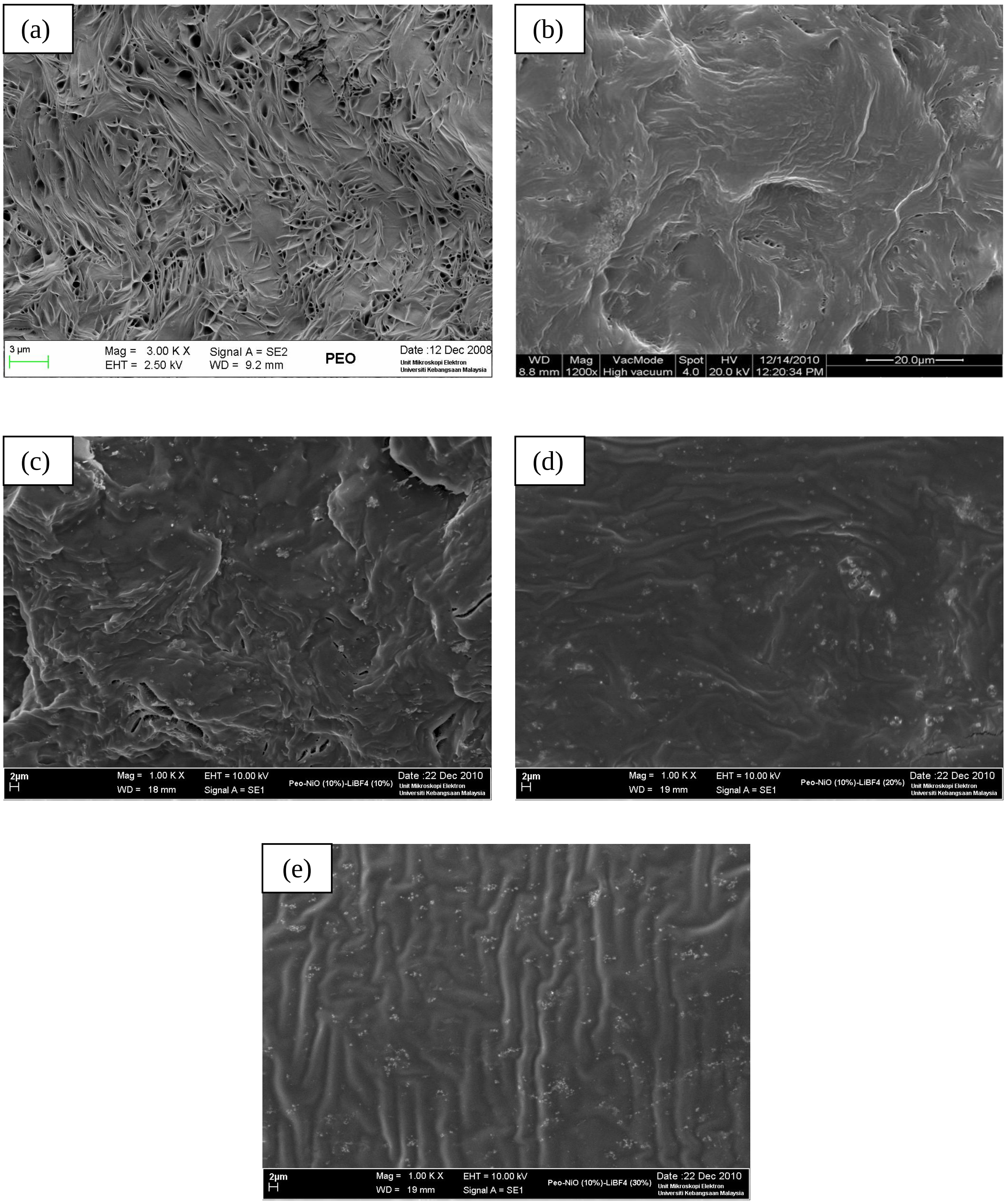

Figure 3. SEM micrographs of (a) pure PEO, (b) PEO-$LiBF_4$, PEO-NiO with (c) 10 wt. % $LiBF_4$, (d) 20 wt. % of $LiBF_4$ and (e) 30 wt. % $LiBF_4$

4. CONCLUSIONS

Composite polymer electrolyte based on PEO-NiO-$LiBF_4$ system was prepared via solution casting technique. The effect of $LiBF_4$ salt concentration on the ionic conductivity, crystallinity degree and morphology of PEO based composite polymer electrolyte was investigated by AC impedance spectroscopy, XRD and SEM, respectively. The x-ray diffraction confirms the reduction of crystalline phase with the addition of salt. NiO particle were found to be well distributed in the polymer matrix and the rough surface of PEO becomes smooth due to the addition of salt based on the observation from SEM. From the impedance analysis, the ionic conductivity was found to increase with wt. % salt up to a maximum value. The conductivity reached the maximum value of 8.75×10^{-4} $\mathrm{Scm^{-1}}$ at 30 wt. % $LiBF_4$.

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References

1. J.R. MacCallum and C.A. Vincent, *Polymer Electrolyte Reviews 1*, (1987) London, Elsevier.
2. B. Scrosati, J.R. MacCallum and C.A. Vincent, *Polymer Electrolyte Review 1*, 315 (1987). London. Elsevier
3. J.E. Weston and B.C.H. Steele, *Solid State Ionics*, 7 (1982) 75.
4. F. Croce, F. Bonino, S. Panero and B. Scrosati, *Philos. Mag. B.* 5 (1989) 161.
5. B.-K. Choi and K.-H. Shin, *Solid State Ionics*, 303 (1996) 86.
6. A. Loupy and B. Tchoudar, *Salts Effects in Organic and Organic Metallic Chemistry*, (1991) New York, VCH Publishing.
7. O. Mahendran and S. Rajendran, *Ionics*, 9 (2003) 282.
8. M.S. Su'ait, A. Ahmad, M.Y.A. Rahman, *Ionics*, 15 (2009) 497.
9. A.M.M, Ali, M.Z.A. Yahya, H. Bahron and R.H.Y. Subban, *Ionics*, 12 (2006) 303.
10. R.H.Y. Subban, A.M.M. Ali, H. Bahron, T. Winie, F. Latif, M.Z.A. Yahya, *Ionics*, 14 (2008) 491.
11. F.M. Gray, *Polymer Electrolytes*, (1997) London: RSC Material Monographs.
12. M.D. Glasse, R. Idris, R.J. Latham, R.G. Linford and W.S. Schlindwein, *Solid State Ionics*, 147 (2002) 289.
13. R.H.Y. Subban and A.K. Arof, *J. New Materials for Electrochemical Systems*, 6 (2003) 197.
14. R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura and T. Hattori, *Solid State Ionics*, 177 (2006) 2679.
15. H.X. Wang, Z.X. Wang, H. Li, Q.B. Meng and L.Q. Chen, *Electrochim Acta*, 52 (2006) 2039.
16. R. Idris, M.D. Glasse, R.J. Latham, R.G. Linford and W.S. Schlindwein, *J. Power Sources*, 94 (2001) 206.
17. Y. Alias, I. Ling and K. Kumutha, *Ionics*, (2005) 11 (2005) 414.
18. P.P. Chu and M.J. Reddy, *J. Power Sources*, 115 (2003) 288.
19. Z. Tang, J. Wang, Q. Chen, W. He, C. Shen, X.X. Mao and J. Zhang, *Electrochim Acta*, 52 (2007) 6638.
20. S.A.M. Noor, A. Ahmad, I.A. Talib, M.Y.A. Rahman, *Ionics*, 16 (2010) 161.
21. M.S. Su'ait, *Preparation and characterization of MG49 based SPE*, (2010) M.Sc. thesis, UKM Bangi Malaysia.
22. E.Z. Monikowska, Z. Florajnmezyk, E. Jonska, *J. Power Sources*, 173 (2007) 734.