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Effect of NiO nanofiller concentration on the properties of PEO-NiO-LiClO$_4$ composite polymer electrolyte

E. M. Fahmi · A. Ahmad · M. Y. A. Rahman · H. Hamzah

Abstract Composite polymer electrolyte films comprising polyethylene oxide (PEO) as the polymer host, LiClO$_4$ as the dopant, and NiO nanoparticle as the inorganic filler was prepared by solution casting technique. NiO inorganic filler was synthesized via sol-gel method. The effect of NiO filler on the ionic conductivity, structure, and morphology of PEO-LiClO$_4$-based composite polymer electrolyte was investigated by AC impedance spectroscopy, X-ray diffraction, and scanning electron microscopy, respectively. It was observed that the conductivity of the electrolyte increases with NiO concentration. The highest room temperature conductivity of the electrolyte was 7.4×10^{-4} S cm^{-1} at 10 wt.% NiO. The observation on structure shows the highest conductivity appears in amorphous phase. This result has been supported by surface morphology analysis showing that the NiO filler are well distributed in the samples. As a conclusion, the addition of NiO nanofiller improves the conductivity of PEO-LiClO$_4$ composite polymer electrolyte.

Keywords Ionic conductivity · Poly(ethylene oxide) · Nickel oxide · Lithium perchlorate · Composite polymer electrolyte

Introduction

Composite polymeric electrolytes are a new class of materials that combine the properties of inorganic particles with the processability and flexibility of an organic polymer matrix.

The resulting hybrid materials offer the possibility of a new generation of nanostructured materials with diverse applications such as electronic or photonic devices, sensors, and catalysts [1–3]. There are a broad variety of available polymers that can be used to prepare nanocomposites. Poly(ethylene oxide) (PEO) has been one of the most widely studied in the last decade due to its electrochemical stability. The basic assumption in several investigations has been that the polymers, by virtue of very high molecular weights, still provide high oxygen to metal ratio for salt in polymer which is significantly higher than the normal four or six required for full coordination of Li$^+$ ions [4]. Similarly, nickel oxide (NiO) has been under extensive investigations for the last few years as an important inorganic material in several applications. It has been reported in batteries, electrochromic material, catalysts, electrodes, gas sensor, and in electronic industry [5–9]. Polymer/NiO composites in different polymer matrices have been prepared for applications as magnetic materials [10], gas sensors [11], and light-emitting and electronic devices [12]. In this work, we prepared a composites polymeric electrolyte of PEO-LiClO$_4$ with NiO as filler that was synthesized via sol-gel method. The electrolyte samples were characterized by AC electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and X-ray diffraction (XRD) to investigate the effect of the filler concentration on the conductivity, morphology, and structure of the electrolyte, respectively.

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Experimental

The host materials, PEO (M_w=600.00) was obtained from Sigma-Aldrich, tetrahydofuran (THF; SYSTERM; ChemAR, Kielce, Poland), LiClO$_4$ (Fluka/Sigma-Aldrich, St. Louis, MO, USA), and nanosized NiO filler with grain size ~400 nm and purity of 99.9%. The preparation of NiO nanofiller used Ni(NO$_3$)$_2$.6H$_2$O (99.9%) as a raw material. It

was dissolved into deionized water and the mixed solution was heated at 70 °C with mechanical stirring for about 24 h. After the removal of water through evaporation, a translucent green gel was formed. Next, the gel obtained was aged and dried at 110 °C for 24 h; subsequently, it was calcined at 500 °C for 6 h.

To prepare the composite polymer electrolyte film, three grams of PEO was dissolved into 80 ml THF and stirred using a magnetic stirrer at 55 °C for 24 h to obtain a homogenous solution. Various wt.% nanosized NiO were dissolved separately in THF and mixed together with the PEO solution and stirred efficiently for 24 h to achieve a homogenous mixture. Then, 20 wt.% LiClO$_4$ was dissolved separately in THF and poured into the mixed solution and further stirred for another 12 h before the casting process. The electrolyte solution was cast onto a teflon mold and the solvent were allowed to slowly evaporate in a fume hood at room temperature. Residual solvents were further removed in a vacuum oven for 24 h at 50 °C. The samples were stored in a desiccator until further use.

The morphology of the samples was characterized by using SEM model model Philips XL30 with 3,000× magnification for the surface morphology and 100,000× magnification to observe the size of NiO dispersed in the electrolyte. Morphology studies were carried out to investigate the effect of NiO filler content on the surface morphology of the PEO-LiClO$_4$. The 25 kV accelerating voltage was used in the characterization. FESEM analysis was done at the fractured with the gold sputtered-coated film. The impedance measurements were carried out using high frequency response analyzer (HFRA Solartron 1255, Sclumberger) and electrochemical interface (SI1286) in the frequency range of 100 Hz to 1 MHz with 30 mV amplitude. The ionic conductivity measurements were carried out with the aim to observe the effect of nanosized NiO filler addition on the electrical properties of the electrolyte system. The composites polymer electrolytes were sandwiched between the stainless steel ion blocking electrodes with a surface contact area of 2.0 cm^2. The EIS analysis was conducted at room temperature. XRD model PANalytical (Model PW3040/60 X'pert Pro MPD) was used to observe the crystalline or the amorphous phase as a function of salt content. The structure and crystallization of polymer salts complex was determined by observing the appearance and disappearance of the crystalline or amorphous regions. The data were collected from the range of diffraction angle 2θ from 2° to 80° at the rate 0.04° s^{-1}.

Results and discussion

Ionic conductivity The typical impedance spectra of the electrolytes are shown in Fig. 1. The bulk resistance of all
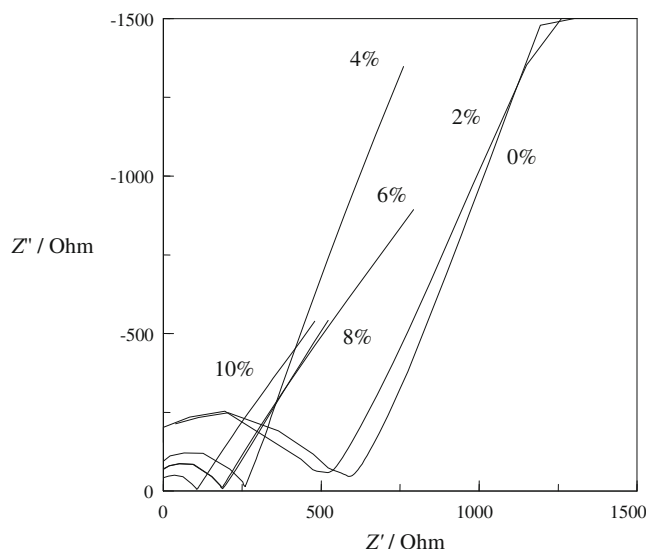

Fig. 1 Impedance spectra of PEO-LiClO$_4$ with different weight percentage of NiO

electrolyte samples was analyzed from Fig. 1 and illustrated in Table 1. The complex impedance spectra show two well-defined regions, a semicircle in the high frequency range which is related to the conduction process and the linear region in the low frequency range that is attributed to the bulk effect of blocking electrodes. The behavior of dielectrics under the application of steady voltage is mainly dependent on the type of contacts between the metal electrodes and the dielectric material. Therefore, the observed transient current was due to the polarization of the material, which had been caused by the hopping of positive or negative charges in the polymer electrolyte system [13].

Figure 2 shows the variation of the room temperature conductivity of PEO-NiO-LiClO$_4$ electrolyte with NiO concentration. The conductivity increases linearly with the NiO content from 0 to 10 wt.% NiO. The lowest conductivity is 1.7×10^{-5} S cm^{-1} obtained at 0 wt.% NiO, while the highest value is 7.4×10^{-4} S cm^{-1} due to the addition of 10 wt.% NiO filler. These observations are supported with the finding reported in [8] for the polymer electrolyte system of PEO-ZnO. They found that the addition of ZnO filler

Table 1 Bulk resistance of PEO-NiO-LiClO$_4$

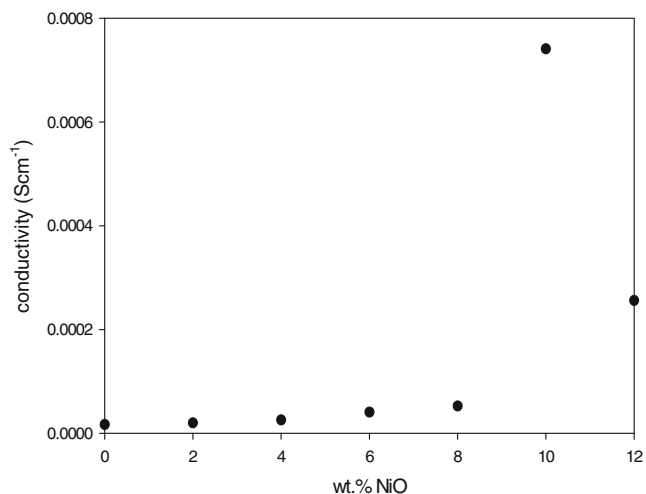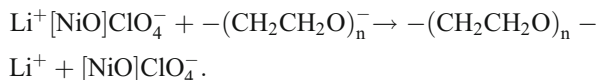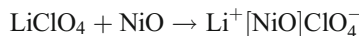| wt.% NiO	Thickness, l (cm)	Resistance, R_b (Ω)
0	0.015	445.78
2	0.015	372.86
4	0.021	405.58
6	0.020	243.50
8	0.026	246.24
10	0.021	141.04
12	0.026	504.67

Fig. 2 Variation of PEO-NiO-LiClO$_4$ conductivity with NiO content

increased the ionic conductivity of the PEO-based polymer electrolyte system. They claimed that the addition of filler increased the degree of amorphous phase through the Lewis acid–base interactions with the PEO chains, thus increasing the ionic conductivity. Once the NiO contents increases above 10 wt.%, the conductivity decreases. The LiClO$_4$ salt which was fixed at 20 wt.% serve as ions sources. The decrease of ionic conductivity is due to the filler properties that have a certain blocking effect on a long range of ion transport for the conduction pathway. The decrease in the conductivity occurs when 12 wt.% NiO was added into the polymer composite, resulting in the conductivity of 2.6×10^{-4} S cm^{-1}. The

schematic presentation of chemical reactions and interactions in the electrolyte composite are as follows;

$$LiClO_4 + NiO \rightarrow Li^+[NiO]ClO_4^-$$

$$Li^+[NiO]ClO_4^- + -(CH_2CH_2O)_n^- \rightarrow -(CH_2CH_2O)_n - Li^+ + [NiO]ClO_4^-.$$

Furthermore, an increase of ionic conductivity with NiO content also attributed with a reduction of crystallinity of composites polymer electrolytes. A reduction of crystallinity arises from random distribution of fine NiO powder which may introduce the topological disorder in the electrolyte. A polymer chain in the amorphous phase is more flexible, which results in an increase of segmental motion of the polymer [14]. Another factor enhancing the electrolyte conductivity is the oxygen concentration of the NiO dopants. Sample with 10 wt.% NiO has the highest oxygen vacancy concentration compared with the other samples and the OH group may prevent its NiO atoms from contacting with the polymer electrolyte so that the interactions between NiO and PEO-LiClO$_4$ are stronger, leading to higher conductivity of the electrolyte [15].

Structural studies Figure 3 shows the XRD patterns of composite polymer electrolyte films with various concentration of NiO as well as for pure PEO and NiO filler. The appearance of amorphous region or the reduction of crystalline region would give a high ionic conductivity as com-

Fig. 3 XRD diffractogram pattern of **a** PEO, **b** LiClO$_4$, **c** NiO and PEO-LiClO$_4$ with different weight percent of NiO: **d** 0%, **e** 2%, **f** 4%, **g** 6%, **h** 8%, and **i** 10%
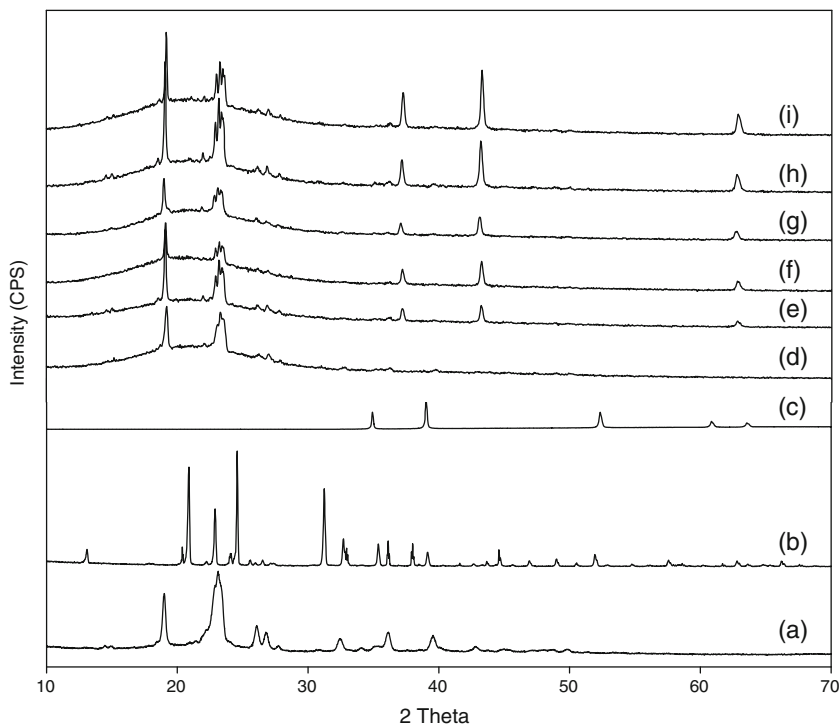
pared to the crystalline or semicrystalline region as reported elsewhere [16–21]. The indexing of the two PEO peaks is reported to be at 19.5° and at 23.5° of monoclinic system [22]. The characteristic diffraction peaks of crystalline PEO are apparent between $2\theta = 15°–40°$ [23, 24]. The two prominent peaks for PEO at $2\theta = 19.1°$ and 23.1° are present in all the patterns indicating the presence of pure polymer. Nevertheless, the diffractogram show that the intensities of the NiO peak increases with wt.% NiO and the intensity of the PEO peaks decreases and become broader. The broadening of sharp peaks of PEO could be due to the disruption of the PEO crystalline structure by LiClO$_4$ and indicates that

complexation has taken place in the amorphous phase [15]. The results show both the decrease in degree of crystallinity and the lamellae size of PEO in the presence of Li salt [25]. The main XRD peaks of PEO are characterized by significant changes in the full width at half maximum (FWHM) with increasing filler concentration. The peak broadening estimated in terms of FWHM has been used to evaluate the Scherrer length (l) of the main PEO peak. This Scherrer length was automatically calculated using X'Pert HighScore software with Scherrer formula $(l) = [0.9 \ ]/[B\cos\theta_B]$ where is the wavelength of the X-rays and FWHM in radians. The l of main PEO peaks was 21.1 nm.

Fig. 4 SEM micrograph of **a** PEO **b** NiO particles and PEO-LiClO$_4$ with different weight percent of NiO: **c** 2%, **d** 4%, **e** 6%, **f** 8%, and **g** 10%
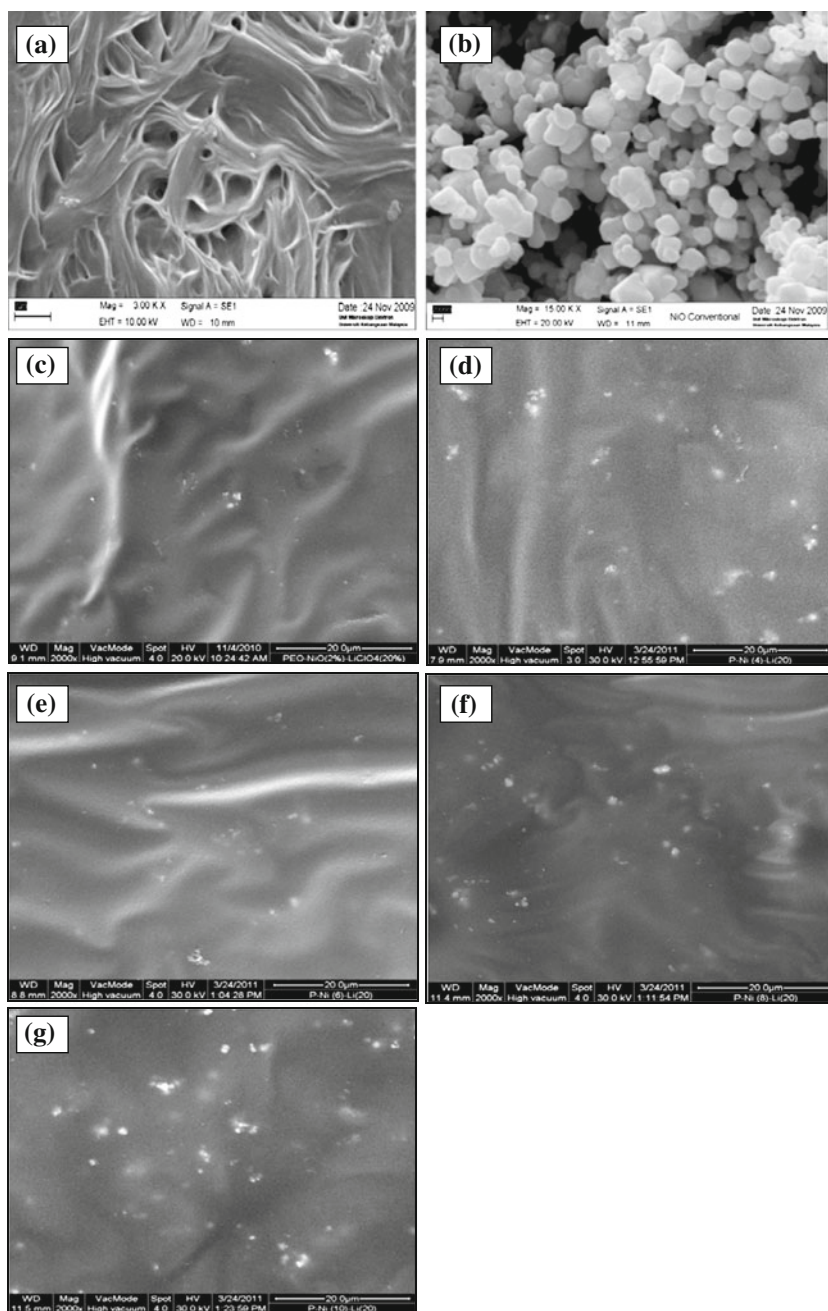
This value decreased to 16.5 nm at 10 wt.% NiO. The Scherrer length characterizes the crystallite size of PEO and it gives a picture of change in the PEO crystallinity upon the filler addition. These results suggested that the degree of crystallinity of PEO decreased with the NiO content.

SEM analysis Figure 4 shows the SEM micrographs of nanocomposite polymer electrolytes with and without NiO filler, respectively. According to [26], the pure PEO film possesses a rough surface morphology as shown in Fig. 4a. Figure 4b shows the morphology of the NiO filler whose particles are well distributed in the entire surface region. This result is consistent with the literature reported in [27]. However, the rough surface of PEO was completely changed and the surface morphology of polymer electrolyte becomes smooth with the addition of NiO filler as shown in Fig. 4c–g. The reduction of PEO crystallinity arises from random distribution of NiO filler 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 [26]. Thus, the conductivity of PEO-based polymer electrolytes increases with wt.% NiO which is supported by the XRD results.

Conclusions

A composite polymer electrolyte of PEO-LiClO$_4$ with nano-sized NiO filler has been prepared by solution casting technique. Ionic conductivity, structural and morphological properties of composite polymer electrolyte PEO-LiClO$_4$ as a function of NiO concentration has been investigated. The highest room temperature conductivity of the electrolyte of 7.4×10^{-4} S cm^{-1} was obtained at 10 wt.% NiO. The increase in conductivity of the electrolyte with the NiO filler concentration was explained in terms of its structure and surface morphology. Further research is to be carried out in order to improve the conductivity of the PEO-NiO-LiClO$_4$ electrolyte to make it suitable for ionics device applications.

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