Research Article

Ionic Conductivity and Interactions in Sodium ion Conducting Solid Polymer Electrolytes Based on Poly (Ethylene Oxide)

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Abstract

In this work, we have investigated the ion transport properties and the structure of a Na-ion conducting solid polymer electrolyte based on polyethylene oxide. Sodium perchlorate, $NaClO_4$, was used as the salt. The electrolyte samples were synthesized using common solvent casting method varying the polymer and salt compositions. The prepared samples were characterized using three techniques. The impedance spectroscopy was used to calculate the ionic conductivity whereas FTIR spectroscopy was used to identify the ion-ion and ion-polymer interactions. The polarization microscopy was used to analyze the morphology and the crystallinity of the samples. Our results showed that the maximum ionic conductivity of 1.01×10^{-4} Scm^{-1} at room temperature can be obtained with the electrolyte having PEO: $NaClO_4$ 20:1 molar ratio. The collected polarization micrographs showed a remarkable change in surface mophology and crystallinity of the electrolytes with different salt concentrations. Further, analyzed FTIR spectra indicated that there is a small but clear influence on the vibrational modes of the polymer backbone after addition of the salt.

Keywords: Solid polymer electrolytes, PEO, Ionic conductivity, Interactions

1. Introduction

Recent rechargeable battery research efforts are mainly focused on Sodium-ion batteries (SIBs) compared to traditional Lithium-ion batteries (LIBs) since available global lithium resources will not be sufficient to meet the ever increasing demand for portable power sources (Yabuuchi *et al.*, 2014). Further, lithium resources are mainly distributed (around 75% of the global deposits) in some politically unstable South American countries, which compels the global

battery market to depend on these countries for the importation of lithium raw materials (Pan *et al.*, 2013). Due to the natural abundance and relatively lower cost of sodium raw materials, sodium based rechargeable battery would be a viable alternative to expensive LIBs.

Any rechargeable battery mainly consists of three parts i.e. anode, electrolyte, and cathode. Among these three components, the electrolyte plays a major role for ion conduction from cathode to anode and vice versa. The electrolyte is typically made of dissolving an ionic salt in an appropriate ion transporting medium and can be formed mainly as a liquid or a solid. Even though liquid electrolytes exhibit high ionic conductivity, they have a high risk of leakage and electrode corrosion. However, solid electrolytes do not have such problems. Among different strategies used to fabricate solid electrolytes, polymer based solid electrolytes have several advantages such as light weight, flexibility and absence of leakage of electrolyte, compared to the conventional liquid electrolytes (Barbosa *et al.*, 2011).

In this work, we synthesized a solid polymer electrolyte based on poly (ethylene oxide) (PEO) and a sodium salt i.e. $NaClO_4$. The developed materials were characterized using complex impedance spectroscopy to determine the ionic conductivity whereas FTIR spectroscopy was used to identify the ion-ion and ion-polymer interactions. The morphology and crystallinity of the samples were analyzed using polarization microscopy.

2. Methodology

The polymer electrolytes were synthesized using common solvent casting method. Prior to use, PEO and salt ($NaClO_4$) were vacuum dried at 50°C and 120°C respectively. Appropriate quantities of PEO and $NaClO_4$ were mixed as oxygen to Na^+ molar ratios were n:1, where n = 80, 60, 50, 40, 30, 20 and 15. Mixtures were dissolved in acetonitrile and stired well for 24 hours at room temperature and the slurry was cast on a Teflon support. Prio to take measurements, the prepared electrolyte films were vacuum dried over 24 hours. In order to study the temperature dependence of ionic conductivity, the complex impedence measurements were carried out using SI 1260 Impedance/Gain-Phase analyzer varying the temperature from room temperature (25°C) to 85°C. The surface morphology and polymer-salt interactions of some selected samples have been studied using polarization microscopy and FTIR spectroscopy respectively.

3. Results and Discussion

The temperature dependence of ionic conductivity for the solid polymer electrolytes $(PEO)_n$ $NaClO_4$ (n = 80, 60, 50, 40, 30, 20 and 15) is shown in Figure 1(A).
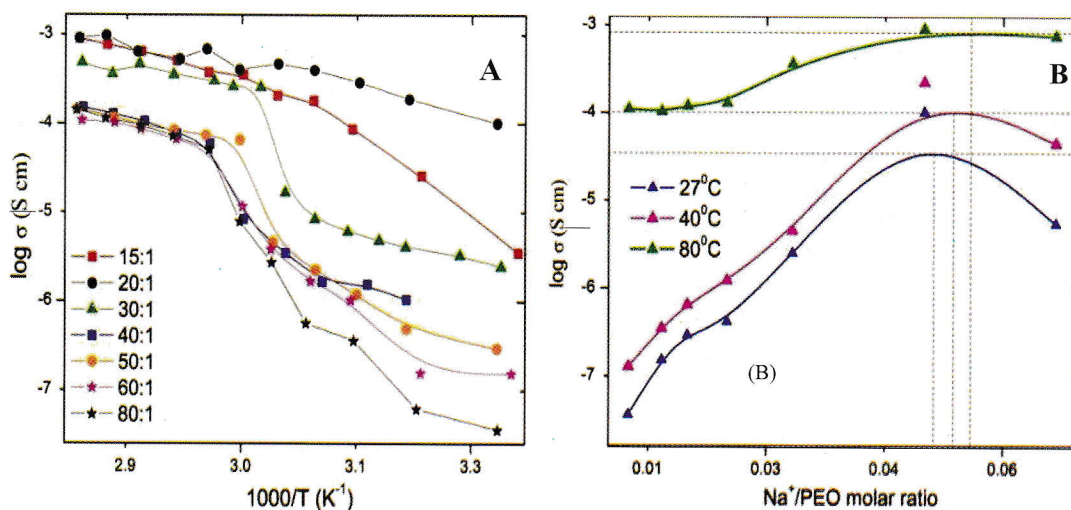

Figure 1: (A) Variation of ionic conductivity with inverse temperature for the polymer electrolyte samples, $(PEO)_nNaClO_4$ (n = 80, 60, 50, 40, 30, 20 and 15). (B) Conductivity isotherms for some selected temperatures, 27°C, 40°C and 80°C.

It is clear from this Figure that the electrolyte $(PEO)_{20}NaClO_4$ shows the highest ionic conductivity at room temperature (25°C). The room temperature conductivity of the sample $(PEO)_{20}NaClO_4$ is 1.01×10^{-4} Scm^{-1}. The plot of the variation of conductivity versus Na^+/PEO molar ratios at various temperatures (conductivity isotherms) is shown in Figure 1(B). These results also indicate the highest ionic conductivity for the sample $(PEO)_{20}NaClO_4$ for different temperatures.

A closer inspection of the curves of Figure 1(A) reveals that the semi-crystalline to amorphous phase transition occurs around 60°C and much greater conductivity enhancement occurs in the crystalline phase compared to that of amorphous phase. The crystalline to amorphous phase transition of the samples $(PEO)_nNaClO_4$ (n= 80, 60, 50, 40 and 30) is much more visible compared to the samples of $(PEO)_{15}NaClO_4$ and $(PEO)_{20}NaClO_4$ and this transition has almost disappeared for those two samples. This is revealed that the ionic conductivity of electrolytes, $(PEO)_{15}NaClO_4$ and $(PEO)_{20}NaClO_4$, does not follow the Arrhenius type but Vogel-Tamman- Fulcher (VTF) behavior indicating their amorphous nature (Ingvar *et al.*, 1994).

Figure 2 shows the polarization micrographs of the samples, $(PEO)_n NaClO_4$ (n=20, 30 and 60) together with pure PEO. This comparision of the surface morphology shows a remarkable change in the surface properties and texture of polymeric thin films with different salt contents. The concentration (size) of spherulites decreases (increases) with increase of salt concentration, having larger spherulites for the $(PEO)_{20} NaClO_4$. These results clearly shows the increment of amorphous phase content of the sample and favors decreasing the crystallinity by preventing agglomeration of the polymer chains. Thus, the transition of the semi-crystalline to amorphous phase is discussed above in conductivity results can be further confirmed with the aid of these micrographs.
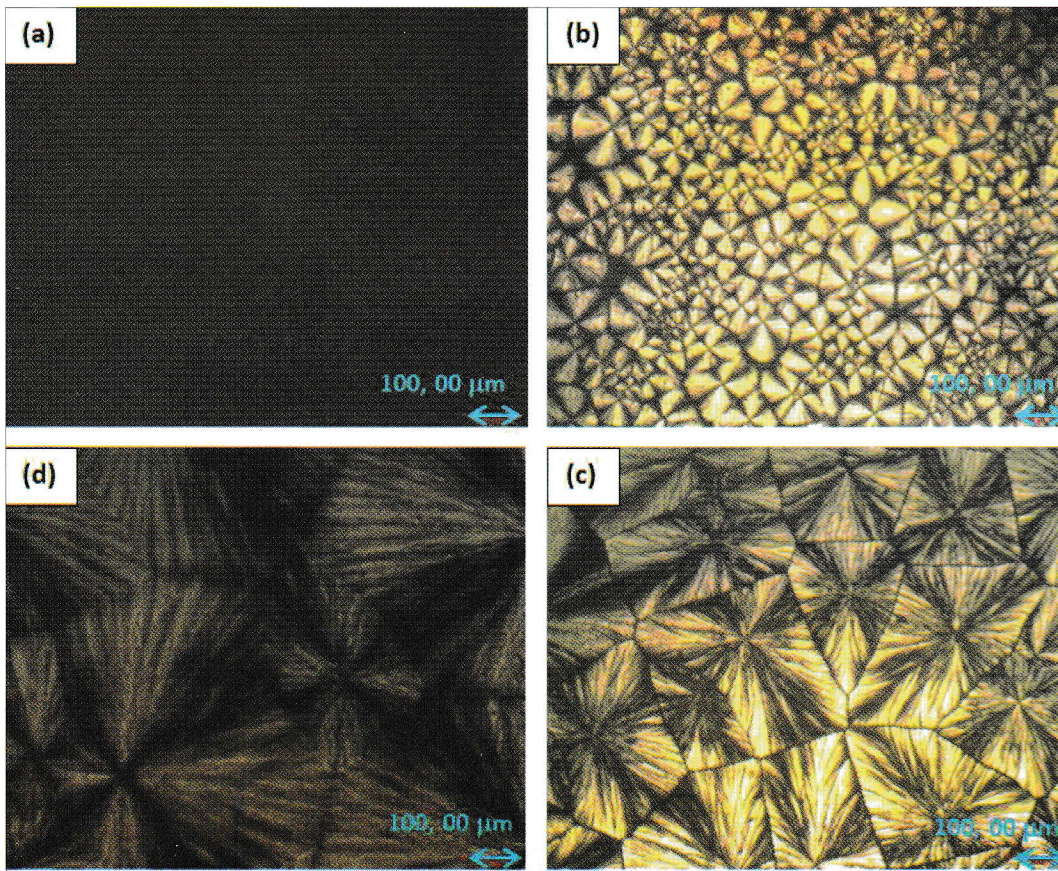

Figure2: Polarization micrographs of some selected electrolytes, [a] $(PEO)_{20} NaClO_4$ [b] $(PEO)_{30} NaClO_4$ [c] $(PEO)_{60} NaClO_4$, and [d]100% PEO.

In order to understand the nature of the charged transport of the sample with highest conductivity, the DC polarization test was carried out with the blocking electrodes (stainless steel, SS) using a cell, SS/electrolyte/SS and collected results without fitting are shown in Figure 3. The electronic transference

number of the DC polarization test of the electrolyte $(PEO)_{20}NaClO_4$ is 0.0075. This indicates that the conduction is predominantly due to ions rather than electrons (Kumar *et al.,* 2010)
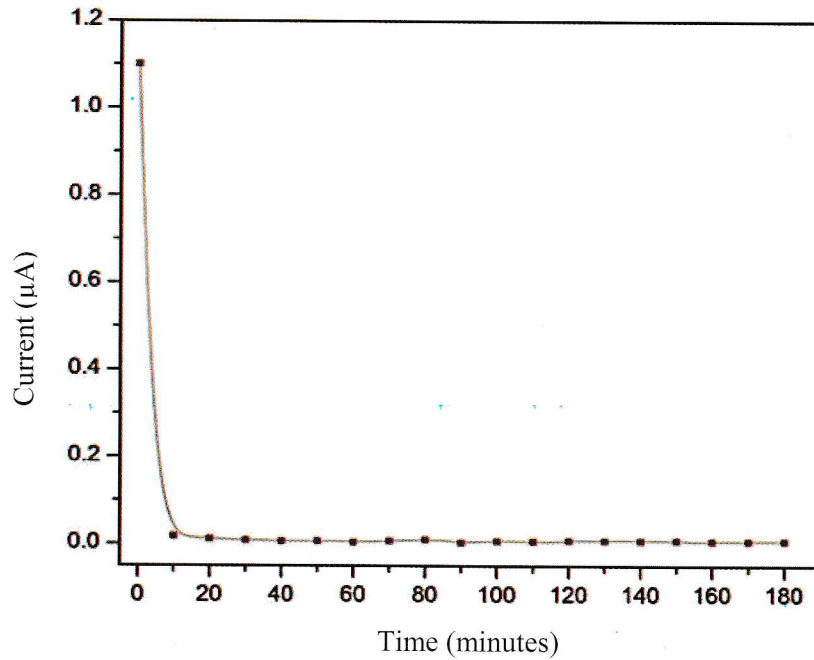

Figure 3: DC Polarization test results of $(PEO)_{20}NaClO_4$

FTIR spectra can provide qualitative information on both structural changes of the polymer in the electrolyte and interactions between salt and the polymer (Arup *et al.,* 2011 and Dissanayake *et al.,* 1995). Figure 3 shows the FTIR spectrums of the $(PEO)_nNaClO_4$ electrolytes (n= 60, 30, 20 and 15) alone with pure PEO in the region of 1160-1020 cm^{-1} around the C-O-C vibrational mode of the PEO (Christopher Arup *et al.,*1999). The sample with high crystallinity, $(PEO)_{60}NaClO4$, shows almost similar spectral shape as seen in pure PEO. In addition, the shape of the peak for other three samples has clearly broadened while they have small differences between each other. These spectra indicate that there is a small but clear influence on this vibrational mode when the salt concentration change in the PEO:salt complex.
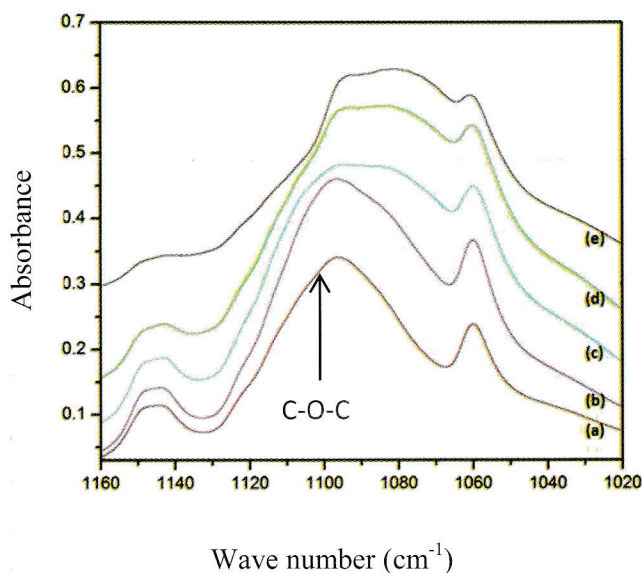
Figure 4: FTIR spectrums of $(PEO)_nNaClO_4$ electrolytes (a) pure PEO, (b) n=60, (c) n=30, (d) n=20 and (e) n=15 in the region around the C-O-C mode of the PEO. The spectra have been vertically offset for clarity.

Conclusion

In this work, we synthesized and characterized Na^+ ion conducting solid polymer electrolytes based on PEO polymer. The Na-ion conduction was obtained by incorporating appropriate quantities of $NaClO_4$ into the polymer with oxygen to Na^+ molar ratio, n:1, where n= 80, 60, 50, 40, 30, 20 and 15. In the $(PEO)_nNaClO_4$ polymer salt complex, the highest ionic conductivity is observed for the system $(PEO)_{20}NaClO_4$. The polarization micrograhs shows a remarkable change in the surface properties and texture of polymeric thin films with different salt contents. In addition, FTIR spectra indicate that there is a small but clear influence on the vibrational modes of the polymer for different PEO:salt complexes.

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