Synthesis and characterization of sodium ion conducting solid polymer electrolytes based on poly (ethylene oxide)

W.A.A.E.B. Wanithunga, H.M.J.C. Pitawala *
Faculty of Science and Technology, Uva Wellassa University of Sri Lanka

and

V.A. Seneviratne
Department of Physics, University of Peradeniya, Peradeniya,

Introduction

Developments of novel ion conducting materials for energy storage devices are presently receiving much attention due to demand of energy. Among different strategies, polymer based solid electrolytes have several advantages such as light weight, flexibility and absence of leakage of electrolyte, compared to the conventional liquid electrolytes (Gray, F. M., 1991). In this work, synthesis of poly (ethylene oxide) (PEO) based sodium ion conducting electrolytes and characterization them using complex impedance spectroscopy, polarization microscopy, and FTIR spectroscopy are discussed.

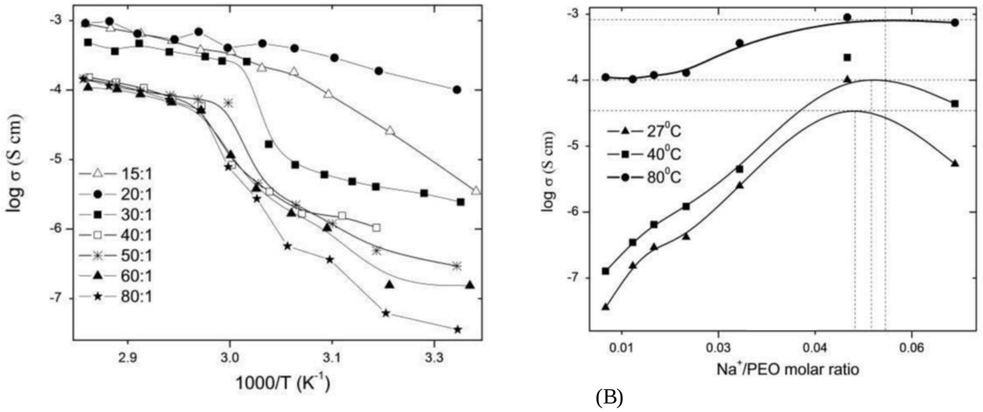
Methodology

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 keeping the oxygen to Na^+ molar ratios as n:1, where n=80, 60, 50, 40, 30, 20, and 15. Mixtures were dissolved in acetonitrile and stirred well for 24hrs at room temperature and the slurry was cast on a Teflon support. Prior to take measurements, the prepared electrolyte films were vacuum dried over 24 hrs. In order to study the temperature dependence of ionic conductivity, the complex impedance measurements were carried out. The surface morphology and polymer-salt interactions of some selected samples have been studied using polarization microscopy and FTIR spectroscopy respectively.

Results and Discussion

The temperature dependence of ionic conductivity for the solid polymer electrolytes (PEO)n NaClO4 (n=80, 60, 50, 40, 30, 20, and 15) is shown in Figure 01(A). It is clear from this figure that the electrolyte (PEO)20NaClO4 shows the highest ionic conductivity at room temperature(25 °C). The room temperature conductivity of the sample (PEO)20 NaClO4 is 1.01×10^{-4} S cm^{-1}. The plots of the variation of conductivity versus Na^+/PEO molar ratios at various temperatures (conductivity isotherms) is shown in Figure 01(B). These results also indicate the highest ionic conductivity for the sample (PEO)20NaClO4 for different temperatures.

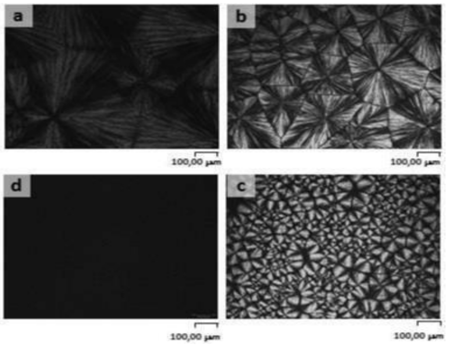
A closer inspection of the curves of Figure 01(A) reveals that the semi-crystalline to amorphous phase transition occurs around 60 °C and that a much greater conductivity enhancement occurs in the crystalline phase compared to that of amorphous phase. The crystalline to amorphous phase transition of the samples (PEO)nNaClO4 (n=80, 60, 50, 40, and 30) is much more visible compared to the samples of (PEO)15NaClO4 and (PEO)20NaClO4 and 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 (Pitawala *et al.*, 2007).



(B)

(A)

Figure 01: (A) Variation of ionic conductivity with inverse temperature for the polymer electrolyte samples, (PEO)n NaClO4 (n=80, 60, 50, 40, 30, 20, and 15). (B) Conductivity isotherms for some selected temperatures, 27 °C, 40°C, and 80°C electrolyte



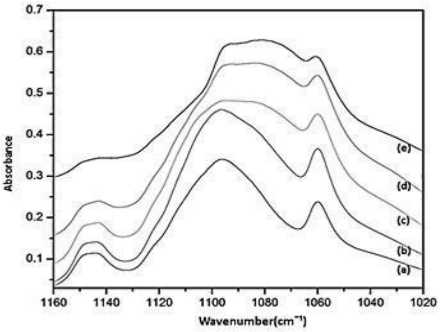


Figure 02: Polarization micrographs of some selected electrolytes, [a](PEO)20NaClO4 [b](PEO)30NaClO4 [c](PEO)60NaClO4, and [d]100% PEO.

Figure 03: FTIR spectrums of (PEO)nNaClO4 electrolytes (a) pure PEO, (b) n=60, (c) n=30, (d) n=20, and (e) n=15 in the region around spectra

Figure 02 shows the polarization micrographs of the samples, (PEO)$_n$NaClO$_4$ (n=20, 30, and 60), together with pure PEO. A 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$_4$. The micrograph of pure PEO does not show clear spherulites may be due to its high crystallinity. 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.

FTIR spectra can provide information on both structural changes of the polymer in the electrolyte and interactions between salt and the polymer (Dissanayake *et al.,*1995; Seneviratne *et al.,* 2002). Figure 03 shows the FTIR spectrums of the (PEO)$_n$NaClO$_4$ electrolytes (n=60, 30, 20, and 15) alone with pure PEO in the region around the C-O-C vibrational mode of the PEO.

The sample having high crystallinity, (PEO)$_{60}$NaClO$_4$, 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. However, more work should be done for detail analysis of these interactions.

In order to understand the nature of the charged transport of the sample having highest ionic conductivity, the DC polarization test was carried out using the stainless steel (SS) blocking electrodes in a cell, SS/electrolyte/SS (graph is not shown here). According to the results, the electronic transference number of the electrolyte (PEO)$_{20}$NaClO$_4$ is 0.0075. This indicates that the charge conduction is predominantly due to ions rather than electrons.

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)$_n$NaClO$_4$ 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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