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Ionic conductivity enhancement in PEO:CuSCN solid polymer electrolyte by the incorporation of nickel-chloride



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K. Vignarooban ^{a,b}, M.A.K.L. Dissanayake ^{a,c,*}, I. Albinsson ^c, B.-E. Mellander ^c

^a Department of Physics and Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka

^b Department of Physics, Faculty of Science, University of Jaffna, Jaffna, Sri Lanka

^c Department of Applied Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden

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ABSTRACT

Copper-ion based solid polymer electrolytes exhibit interesting electrochemical properties, environmental stability and lower fabrication cost compared to lithium ion based systems. Although, poly(ethylene oxide)(PEO)-based solid polymer electrolytes have been extensively studied, those incorporating copper salts have not been explored much. One major drawback in these electrolytes is the low ionic conductivity at room temperature. In this work, we attempted to enhance the ionic conductivity of PEO₉CuSCN polymer electrolyte by the incorporation of NiCl₂. Incorporation of 10 wt% NiCl₂ showed the highest conductivity enhancement with almost two orders of magnitude increase. The ionic conductivity value at 30 °C increased from 3.1×10^{-9} S cm⁻¹ for the NiCl₂-free electrolyte to 1.8×10^{-7} S cm⁻¹ for the 10 wt% NiCl₂ incorporated electrolyte. This was associated with a significant reduction in T_g by about 30 °C from -53 °C for PEO₉ CuSCN to -83 °C for PEO₉ CuSCN + 10 wt% NiCl₂, indicating an increased segmental flexibility of the polymer chains for NiCl₂ added electrolyte.

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1. Introduction

There are intense worldwide thrusts in research and development of electrolyte and electrode materials for rechargeable batteries, mainly because of the increasing demand for these batteries for numerous portable electronic devices such as computers, mobile phones, cameras and electro-optical devices and also for electrical vehicles [1–3]. Development of new electrolytes is one of the key areas for future high energy density rechargeable batteries, and solid polymer electrolytes are being intensively investigated in the past couple of decades due to their many advantages such as flexible geometry to fabricate in any desired configuration, ease of fabrication as thin films, absence of electrolyte leakage, light weight, low cost and improved safety [1,4].

However, most of the polymer electrolyte research results reported in the literature are on lithium ion conducting materials, mainly because of the rapid growth of lithium-ion rechargeable battery market [4]. A large number of research papers have been published on poly (ethylene oxide) based systems such as PEO–LiX ($X = ClO_4^-$, $CF_3SO_3^-$, BF_4^- , PF_6^-) [3, 5–9] polymer–salt complexes. Because of the limited lithium reserves in the world, the price of lithium salts is high and expected to go up in the near future. Therefore, research is now being focused on electrolytes based on sodium, magnesium and copper salts. A number of polymer electrolytes containing copper salts also exhibit interesting electrochemical properties in addition to their environmental stability and lower cost [10]. Another important advantage of cells based on copper salts is the possibility of using copper metal as one of the electrodes [11]. Except these battery applications, polymer electrolytes are also being increasingly used for electrochemical displays and sensors for which polymer complexes based on less reactive metallic ions than lithium, typically copper, would be advantageous [4].

Multivalent polymer-salt complexes offer important prospects for the understanding of the fundamental properties of polymer electrolytes. However, surprisingly, there are only a very few reports available in the literature on copper based polymer electrolytes. In one of the earliest work performed in 1986, Abrantes et al. [12] have studied the $(PEO)_8CuCl_2$ and $(PEO)_8Cu(ClO_4)_2$ polymer complexes and reported ionic conductivity values of 1.2×10^{-9} and 2.0×10^{-5} S cm⁻¹ respectively at room temperature for these two systems. Two years later, Bonino et al. [4] have studied PEO– $Cu(CF_3SO_3)_2$ complexes at various molar ratios of PEO and Cu(CF₃SO₃)₂. They did ac impedance analysis and dc polarization studies and reported that the system is predominantly an anionic conductor. Thermal and electrical properties of PEO-Cu(ClO₄)₂ polymer electrolytes were studied by Magistris et al. [13] over the $Cu(ClO_4)_2$ concentration range of 0–20 mol% and it was reported that the system has fairly high ionic conductivity almost comparable to that of the corresponding lithium ion systems.

There are a couple of reports published on copper salt complexes formed with polymer hosts other than PEO, such as PAN (poly-



^{*} Corresponding author at: Department of Applied Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden. Tel.: +9481 2232002; fax: +9481 2232131. *E-mail address*: makldis@yahoo.com (M.A.K.L. Dissanayake).

acrylonitrile) and PVA (poly-vinyl alcohol) [10,14]. PAN-CuSCN with EC and PC plasticizers was studied by Perera et al. [10] in 2000 and PVA-Cu(NO_3)₂ polymer complex was studied by Ramya et al. [14] in 2005. It has been reported that 30% Cu(NO₃)₂ doped PVA system has a maximum value for the ionic conductivity, $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. There are very limited number of articles available in the literature on PEO based monovalent copper (Cu^+) salt complexes. Only a couple of papers were published by Sidhu et al. [15,16] on PEO-CuSCN and PEO-CuI and it was reported that these polymer electrolytes are mainly anionic conductors. CuCNS is an unconventional semiconducting material with a band-gap of approximately 3.6 eV [17]. Several compositions of PEO_xCuSCN with different ether oxygen to Cu⁺ ion molar ratios (x %) have been studied and PEO₉CuSCN showed optimum value for the ionic conductivity, although it is too low for practical applications [15].

In the present work, we attempted to enhance the ionic conductivity of PEO₉CuSCN polymer electrolyte by incorporating small amounts of NiCl₂. Since nickel ion conducting materials are electrochemically active and already used in Ni-Cd and Nickel-Metal-Hydride (Ni-MH) batteries, it would be interesting to see how the addition of NiCl₂ will enhance the ionic conductivity in this polymer based PEO:CuSCN solid electrolyte. Also, it has been reported that, in PEO-transition metal chloride complexes (MeCl_n + PEO \rightarrow [MeCl_n - 1....PEO] + Cl), where Me = Cu, Ni, Fe, Co..., the oxygen atoms from polymer play a ligand role and substitute chlorine ligands. Such complex formation leads to the conformational changes in the PEO-salt complex and would influence its ionic conductivity significantly [18]. The effect of NiCl₂ on the ionic conductivity and thermal properties such as glass transition temperature and crystallite melting temperature has been systematically studied in this present work by incorporating different wt% of NiCl₂ (5, 10, 15 and 20) and the 10 wt% NiCl₂ added sample showed best enhancement in ionic conductivity.

2. Experimental

Poly (ethylene oxide) (PEO) (molecular weight, 4×10^{6}) from Polysciences Inc., CuSCN (99%) from Aldrich and NiCl₂ from Vickers Laboratories Ltd. were used as the starting materials. Prior to use, PEO was vacuum dried for 24 h at 50 °C; CuSCN and NiCl₂ both were vacuum dried for 24 h at 200 °C. To prepare the (PEO)₉ CuSCN + x wt% NiCl₂ (x = 0, 5, 10, 15 and 20) polymer electrolytes, appropriately weighed quantities of PEO and CuSCN required for ether oxygen to Cu⁺ ion ratio of 9:1 were dissolved in anhydrous acetonitrile (Aldrich, 99.5%) and was magnetically stirred at room temperature at least for 24 h, until a homogeneous slurry was obtained. Then the slurry was spread onto a Teflon plate and kept inside the fume hood for almost 24 h to allow the solvent to evaporate. Resulting polymer electrolyte film was vacuum dried for 24 h at room temperature to completely remove residual solvent and moisture. Finally, free-standing and visually homogeneous polymer electrolyte films of average thickness 100-200 µm were obtained.

A computer controlled SI 1260 Schlumberger Impedance/Gainphase analyzer (20 Hz–10 MHz) was used to record the impedance spectra on disc shaped samples sandwiched between two springloaded stainless steel blocking electrodes of 13 mm diameter. The temperature of the sample was varied from 25 to 100 °C and the measurements were taken at approximately 10 °C intervals on heating. A thermocouple kept in thermal contact with the sample was used to measure the temperature of the sample. The ionic conductivity was derived from the complex impedance data.

For thermal characterization, Perkin Elmer, Pyris 1 DSC with a heating rate of 10 °C min⁻¹ from -120 °C to 120 °C in the heating cycle was used. Polymer electrolyte films of mass 5–15 mg were sealed in aluminum pans and an empty aluminum pan was used as the reference. Glass transition temperature (T_g) and the crystallite melting

temperature (T_m) were respectively determined from the inflection point and the endothermic peak of the DSC thermogram. Dry N₂ gas was purged over the sample holder to avoid condensation of moisture.

3. Results and discussion

Fig. 1 shows log σ vs 1/T variation for PEO₉CuSCN + x wt% NiCl₂ (x = 0, 5, 10, 15 and 20) polymer electrolyte system at different temperatures ranging from room temperature to 100 °C. All these conductivity values were extracted from the impedance spectroscopic scans taken during the heating cycle. Conductivity isotherms for the same samples are shown in Fig. 2. These data explicitly show that the incorporation of NiCl₂ helped to significantly enhance the ionic conductivity of the PEO₉CuSCN polymer-salt complex and 10 wt% NiCl₂ addition showed the best enhancement at all measured temperatures. log σ vs 1/T variation with temperature (Fig. 1) shows VTF (Vogel-Tamman-Fulcher) behavior, similar to previous reports on a few other copper salt based polymer electrolytes such as $PEO_8Cu(ClO_4)_2$ [12] and PMMA–Cu(CF_3SO_3)₂ [19]. However, there are a few copper based systems reported in the literature which show Arrhenius behavior as well, for example $PEO_xCu(CF_3SO_3)_2$ (x = 10 and 50) polymercopper salt complexes [20].

As shown in Table 1, there is almost two orders of magnitude increase in conductivity due to the addition of 10 wt% NiCl₂. PEO₉CuSCN polymer electrolyte showed a conductivity value of 3.1×10^{-9} S cm⁻¹ at 30 °C, whereas PEO₉CuSCN + 10 wt% NiCl₂ showed a value of 1.8×10^{-7} S cm⁻¹ at the same temperature. Almost the similar conductivity value $(1.2 \times 10^{-9} \text{ S cm}^{-1})$ has been reported by Abrantes et al. [12] for PEO₈CuCl₂ polymer electrolyte at room temperature (25 °C). In the present case, ionic salt CuSCN is an unconventional semiconductor and its band-gap is approximately 3.6 eV [17]. Hopping mechanism between the coordinating sites, local structural relaxations and segmental motions of the polymer chains are the factors contributing to the observed ionic conductivity of these polymer electrolytes. The segmental movement of the polymer facilitates the translational ionic motion. From this, it is clear that the ionic motion is due to translational motion or hopping facilitated by the dynamic segmental motion of the polymer. The polymorphic crystalline structure of the CuSCN, with semiconducting properties is broken down after complexation with the polymer giving rise to solvated Cu⁺ cations and mobile CNS⁻ anions [10]. The ionic character of these electrolytes with anionic contribution can possibly be attributed to these two conducting species.

Fig. 3a and b shows the crystallite melting temperature (T_m) and the glass transition temperature (T_g) respectively for all the samples



Fig. 1. log σ vs 1/T plots for polymer electrolytes incorporating different amounts of NiCl₂; (PEO)₉CuSCN + *x* wt% NiCl₂ (*x* = 0, 5, 10, 15 and 20).



Fig. 2. Conductivity isotherms showing the variation of conductivity with the amount of added NiCl₂ in (PEO)₉CuSCN + x wt% NiCl₂ polymer electrolytes.

studied. As can be seen in Fig. 3a, there is a sharp and narrow peak at the melting point of PEO₉CuSCN polymer electrolyte and this melting peak broadens and T_m drops with the addition of NiCl₂. This is a clear indication that the incorporation of NiCl₂ helps to increase the amorphous phase content of the PEO-CuSCN polymer electrolyte. As the amorphous region increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion to favor inter and intra chain ion hopping, thus increasing the conductivity. Observation of a crystallite melting temperature in PEO-CuSCN polymer electrolytes strongly indicates the two-phase nature, crystalline and amorphous, of these polymer-salt complexes. There are a couple of copper salt based polymer electrolytes reported in the literature which showed single phase amorphous complexes with no T_m. For example PEO₉Cu(CF₃SO₃)₂ polymer electrolytes studied by Dissanayake et al. [21] and PPO-divalent copper halides studied by James et al. [22]. It is useful to recall that the $T_{\rm m}$ for pure PEO is 74 °C [23]. Table 1 summarizes the glass transition temperature (Tg), the crystallite melting temperature (T_m) and the conductivity at 30 °C for all the samples investigated in this study.

It can be seen from Table 1 that the observed conductivity maximum in PEO₉ CuSCN + 10 wt% NiCl₂ correlates with its minimum T_g. This can clearly be realized from Fig. 4, where there is a drop in T_g and an increase in conductivity with the addition of NiCl₂. The 10% NiCl₂ added sample shows lowest T_g (-83 °C) and the highest conductivity (1.8×10^{-7} S cm⁻¹ at 30 °C). Further incorporation of NiCl₂ above 10 wt% (15 and 20 wt%) showed a negative effect resulting a decrease in conductivity and an increase in T_g. This could be due to the blocking of conducting pathways caused by the formation of higher ionic aggregates and clusters at high NiCl₂ concentrations. Correlation between T_g and the conductivity, as illustrated in Fig. 4, strongly suggests that the increased amorphous nature of the polymer electrolyte giving rise to an enhanced segmental mobility for the polymer chains is the quite likely mechanism responsible for the observed conductivity enhancement.

Table 1

Glass transition temperature (T_g), crystallite melting temperature (T_m) and the conductivity at 30 °C for PEO₉CuSCN + x wt% NiCl₂ (x = 0, 5, 10, 15 and 20) polymer electrolyte samples.

Polymer electrolyte	T _g (°C)	T _m (°C)	σ at 30 °C (S cm $^{-1})$
$\begin{array}{l} PEO_9 \text{CuSCN} \\ PEO_9 \text{CuSCN} + 5 \text{ wt\% NiCl}_2 \\ PEO_9 \text{CuSCN} + 10 \text{ wt\% NiCl}_2 \\ PEO_9 \text{CuSCN} + 15 \text{ wt\% NiCl}_2 \\ PEO_9 \text{CuSCN} + 20 \text{ wt\% NiCl}_2 \end{array}$	53 70 83 79 66	68 68 67 66 65	$\begin{array}{c} 3.1 \times 10^{-9} \\ 2.2 \times 10^{-8} \\ 1.8 \times 10^{-7} \\ 7.4 \times 10^{-8} \\ 4.4 \times 10^{-8} \end{array}$



Fig. 3. DSC thermograms taken during the heating run indicating the systematic variation of; (a)Crystallite melting temperature (T_m) . (b)Glass transition temperature (T_g) .

Varying the salt concentration often changes the glass transition temperature of the polymer salt complexes, which invariably appears as the dominant factor affecting the polymer segmental motion and associated ionic mobility [24]. In the present system, the decrease in T_g can be correlated to a decrease in the concentration of transient cross-links, which increases the segmental motion of the polymer chains. Since the segmental motion is rate determining for the mobility of the charge carriers, the conductivity is expected to increase. It is suggested that the two processes, increased segmental mobility which facilitates the mobility of charge carriers and the mobile charge carrier concentration which depends on the nature of the salt and its



Fig. 4. Variation of conductivity at 30 °C (σ_{30}) and the glass transition temperature (T_g) with the amount of incorporated NiCl₂.

interaction with the polymer chains, are optimized for the composition PEO₉ CuSCN + 10 wt% NiCl₂ resulting the maximum conductivity. Significant reduction in T_g by about 30 °C from -53 °C for PEO₉ CuSCN to -83 °C for PEO₉ CuSCN + 10 wt% NiCl₂, clearly supports the idea of increased segmental flexibility of the polymer chains, which would be the driving force for the observed conductivity enhancement.

T_m drops continuously with the amount of incorporated NiCl₂ (Fig. 3a). This continuous drop even for samples with NiCl₂ content higher than 10 wt% strongly suggests that the amorphous phase content is increasing even beyond 10 wt%, but a decrease in conductivity and an increase in T_g have been observed (Fig. 4). The blocking of conducting pathways by higher ionic aggregates could be responsible for the reduction in conductivity. Increase in Tg when the NiCl2 content goes above 10 wt% is a clear indication of this mechanism. The PEO-transition metal complexes containing Cu and Ni salts used in this work can be denoted as $[Cu^+...,PEO] + CNS$ and [NiCl...,PEO] + Cl [18]. The complex formation is expected to lead to conformational changes where helical PEO chains undergo coiling-up and a structure similar to crown ethers (inside which the cation is trapped) is formed. Both cations, Cu⁺ and Ni⁺⁺ as well as the thiocyanate (CNS⁻) and chloride (Cl⁻) anions are expected to contribute to the observed overall ionic conductivity in this system.

According to our observations (Fig. 1), the ionic conductivity of the polymer salt complex increases with increasing NiCl₂ salt concentration up to 10 wt%. This is very likely due to the increase in the number of mobile charge carriers Ni^{++} , Cl^- and charged PEO...Ni complexes formed due to the presence of NiCl₂. In these complexes, the Ni⁺⁺ cation can form coordinating bonds with four oxygen atoms in a PEO segment forming a crown ether-like structure. However, when the NiCl₂ salt concentration increases beyond 10 wt%, the ionic conductivity starts to decrease with NiCl₂ addition. There are several possible factors that can contribute to this effect. Increase in the number of PEO-Ni complexes each with Ni atoms coordinated to four oxygens in the PEO chains would significantly reduce the segmental flexibility of the PEO chain thus restricting the mobility of ionic species in the medium. In addition, the presence of a high concentration of NiCl₂ would lead to the formation of higher ionic aggregates and ionic clusters thereby reducing the mobility of available ionic species. Also, the viscosity of the medium is expected to increase and the amorphous polymeric phase content decreases thus reducing the ionic mobility. All these factors are in agreement with the observed changes in macroscopic properties, such as the ionic conductivity, T_m and T_g shown in Figs. 1, 3a and b, respectively.

4. Conclusions

Since the major drawback in copper–salt based polymer electrolytes is the low ionic conductivity at room temperature, we attempted to enhance the ionic conductivity of PEO₉CuSCN polymer electrolyte by the incorporation of NiCl₂. The addition of NiCl₂ to PEO₉CuSCN decreases the T_g and increases the ionic conductivity up to 10 wt% NiCl₂ addition. A further addition of NiCl₂ above 10 wt% resulted with decreased conductivity and increased T_g. Among various compositions studied, 10 wt% NiCl₂ showed the highest conductivity enhancement and the lowest T_g. Conductivity has been increased by almost two orders of magnitude; 3.1×10^{-9} S cm⁻¹ and 1.8×10^{-7} S cm⁻¹ at 30 °C, respectively for NiCl₂-free and 10 wt% NiCl₂ added samples. A significant reduction in T_g by about 30 °C from -53 °C for PEO₉ CuSCN to -83 °C for PEO₉ CuSCN + 10 wt% NiCl₂ clearly suggests that the increased segmental mobility of the polymer chains is the quite likely mechanism for the conductivity enhancement in this polymer electrolyte system. The observed variations in ionic conductivity can be explained in terms of polymer–salt complex formation which correlates with changes in T_m and T_g of the system.

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