

ELECTRICAL AND THERMAL PROPERTIES OF NANO-COMPOSITE GEL-POLYMER ELECTROLYTES FOR SODIUM-ION SECONDARY BATTERIES

J.H.T.B. JAYAMAHA¹, L. WEWAGAMA¹, K. VIGNAROOBAN^{1,*}, K.S. PERERA², K.P. VIDANAPATHIRANA², M.A.K.L. DISSANAYAKE³, S. SENTHURAN¹, P. RAVIRAJAN¹, M.A. CAREEM⁴ AND A.K. AROF⁴

¹ *Department of Physics, University of Jaffna, Jaffna, Sri Lanka*

² *Department of Electronics, Wayamba University of Sri Lanka, Kuliyaipitiya, Sri Lanka*

³ *National Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka*

⁴ *Center for Ionics, Department of Physics, University of Malaya, Kuala Lumpur, Malaysia*

Corresponding author, e-mail: kvignarooban@gmail.com

ABSTRACT

Research works on Sodium-Ion Batteries (SIBs) are growing rapidly in recent times due to the abundance of sodium raw materials in nature. This work focuses on synthesis and characterization of novel nano-composite gel-polymer electrolytes (NCGPEs) based on Poly (ethylene oxide) (PEO) polymer host and sodium perchlorate (NaClO₄) ionic salt. Among several compositions of PEO:NaClO₄ solid-polymer electrolytes studied in the initial stage of this work, the composition with ether oxygen to Na⁺ ion ratio of 10:1 showed the highest room temperature ionic conductivity (~ 10⁻⁹ S cm⁻¹). Since this conductivity is not good enough for practical applications, we incorporated propylene carbonate (PC) and synthesized gel-polymer electrolytes. Incorporation of 75 wt% of PC and 5 wt% TiO₂ nano-filler into the PEO:NaClO₄ (10:1) composition has led to the formation of NCGPE with highest room temperature ionic conductivity (~ 10⁻⁵ S cm⁻¹). Furthermore, the DC polarization analysis revealed that the electronic transference number (t_{elec}) of these electrolytes are as small as 0.08 for the sample without the filler and 0.17 for the sample with 5 wt% of TiO₂ filler, confirming the dominant ionic conducting nature of these electrolytes. Thermal studies on these electrolytes by using DSC analysis showed that the best conducting NCGPE has the glass transition temperature (T_g) of -14.9 °C.

1. INTRODUCTION

Although the Lithium-Ion Batteries (LIBs) are highly consumed in portable electronic devices such as mobile phones, laptop computers, cameras and also in hybrid and electric vehicles, the limited availability and ever increasing prices of lithium raw materials are the serious concerns for sustaining the mass production of LIBs [1-2]. Hence, secondary batteries beyond lithium-ion are being explored very recently, particularly Sodium-Ion Batteries (SIBs) have become popular especially in the R&D level because of the abundance of sodium raw materials in nature. There are a couple of commercial SIBs in the market too, mainly for stationary energy storage applications for storing the energy from intermittent renewable sources [3-4]. As electrolyte is an important component of these batteries, research efforts on different types of electrolytes are growing exponentially for SIB chemistries. Among several types of electrolytes studied, polymer electrolytes are highly favorable due to the ease of fabrication as thin films, ability to have wide variety of shapes, flexibility to accommodate the volume changes of electrodes during the charging/discharging processes and the ability to form effective electrode-electrolyte contacts [5].

Poly (ethylene oxide) (PEO) is the widely studied polymer host for the preparation of polymer electrolytes, especially for LIB applications, because of its good ion solvation properties. However, most of the sodium-ion conducting gel-polymer electrolytes studied in the past were

based on poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) co-polymer [6-8]. There are a few reports in the literature on PEO based solid-polymer electrolytes for SIBs [9-11]. In 1995, Hashmi *et al.*[9] studied PEO-NaPF₆ solid-polymer electrolytes at several Na⁺ ion to ether oxygen (EO) ratios. The highest room temperature conductivity reported was 5x10⁻⁶ S cm⁻¹ for Na⁺/EO = 0.065 and the temperature dependence of conductivity showed Arrhenius behavior. It was found that the material is predominantly an ionic conductor with ionic transference number of 0.98. In 2013, Pradhan *et al.*[10] investigated PEO-NaClO₄ electrolytes incorporated with SnO₂ filler and PEG (poly-ethylene glycol) plasticizer. In 2015, Nimah *et al.*[11] prepared PEO-NaClO₄-TiO₂ solid-polymer electrolytes by using usual solvent casting technique and studied the structural and electrical properties. They reported a maximum ionic conductivity of 2.62x10⁻⁴ S cm⁻¹ at 60 °C for a composition incorporated with 5 wt% TiO₂.

In this present work, several PEO based solid-polymer (PEO-NaClO₄), gel-polymer (PEO-NaClO₄-PC) and nano-composite gel-polymer (PEO-NaClO₄-PC-TiO₂) electrolytes have been synthesized by systematically varying the weight ratios of PEO, NaClO₄, PC (propylene carbonate) and TiO₂. To the best of our knowledge, there are no reports available on PEO based sodium-ion conducting gel-polymer electrolytes formed with NaClO₄ ionic salt and PC as the solvent. Electrical and thermal properties of these gel-polymer electrolytes have been studied to find out the optimum composition. Reasonably good room temperature conductivity was obtained for the optimized composition.

2. EXPERIMENTAL

2.1 Sample Preparation

PEO (molecular weight, 4x10⁵), NaClO₄ (anhydrous, 99%) and PC (99%) from Sigma-Aldrich (USA) were vacuum dried at 50 °C for 24 hours prior to use. To prepare the PEO-NaClO₄ solid-polymer electrolytes with six different ether oxygen to Na⁺ ion molar ratios, appropriately weighed quantities of PEO and NaClO₄ were first dissolved in acetonitrile (BDH) by magnetically stirring overnight at room temperature until a homogeneous mixture is obtained. The mixture was then poured into a Teflon dish and kept in the fume hood for the solvent to evaporate. Finally, the solid-polymer membranes were vacuum dried at 50 °C for 12 hours. Thereafter, gel-polymer electrolytes have been prepared by adding different weight percentages of PC to the best conducting PEO-NaClO₄ solid-polymer electrolyte composition. In order to enhance the ionic conductivity, different weight percentages of TiO₂ (P-25 Degussa) were also added to the best conducting PEO-NaClO₄-PC gel-polymer electrolyte composition. In order to prepare PEO-NaClO₄-PC-TiO₂ NCGPEs, appropriately weighed quantities of PC and TiO₂ were first dissolved by magnetically stirring for about 1-2 hours at room temperature. Then the required amount of NaClO₄ was added and stirred again at room temperature for about 3-4 hours until the salt homogeneously dissolves into the PC-TiO₂ mixture. Finally, the required amount of PEO was added and magnetically stirred by gently heating at around 100 °C for 4-5 hours until a clear transparent gel is obtained.

2.2 Electrical and Thermal Characterizations

A computer controlled Metrohm PGSTAT128N Autolab Potentiostat/Galvanostat (0.01 Hz - 0.1 MHz) from Metrohm, Netherland was used for impedance measurement on disc shaped samples sandwiched between two spring-loaded stainless steel blocking electrodes separated by a non-conducting spacer. The temperature of the sample was varied from 25 to 65 °C and the

measurements were taken at 5 °C intervals while heating. The ionic conductivity values were extracted from the complex impedance data. DC polarization studies were performed on the samples mounted between the two stainless steel electrodes as described above. Variation of current with time was measured when the sample assembly was under a constant applied DC voltage of 1 V. DSC analysis was performed on best conducting sample by using model Q200 DSC from TA Instruments, USA. Aluminum pans were used to contain about 5 mg of the NCGPE sample under static nitrogen gas environment. Heating/cooling rates used were 20 °C/min and the scan was performed in the temperature range (-80) to 80 °C.

3. RESULTS AND DISCUSSION

Fig.1 shows the conductivity variation with PEO/Na⁺ molar ratio at nine different temperatures (25, 30, 35, 40, 45, 50, 55, 60 and 65 °C) for PEO-NaClO₄ solid-polymer electrolytes. It could be noted that at high salt concentrations (low PEO/Na⁺), conductivity is very low mainly due to the formation of ionic clusters. Similarly, conductivity is also low at low salt concentrations (high PEO/Na⁺), possibly due to the high viscosity of the medium and less number of mobile ions present in the electrolyte. Conductivity is maximum (10⁻⁹ S cm⁻¹ at room temperature) at the PEO/Na⁺ molar ratio of 10, where concentration of ions and the viscosity of the medium reach optimum balance so that the mobility of the ions is optimized. All the solid-polymer electrolytes studied in this work showed Arrhenius behavior of conductivity variation with inverse temperature. Hashmi *et al.*[9] reported Arrhenius behavior for a similar electrolyte system; PEO-NaPF₆. Increase in conductivity with temperature is believed to be due to the expansion of the polymer matrix leading to increase in free-volume. The increased free-volume in turn promotes the mobility of the polymer segments and ionic species, resulting in higher conductivity.

In 2015, Nimah *et al.*[11] confirmed by XRD studies that the PEO-NaClO₄ blends have both crystalline and amorphous regions and they also suggested that the degree of crystallinity of the PEO backbone decreases with the addition of NaClO₄ salt. This decrease of the degree of crystallinity may also result in increased segmental motion of the polymer chains leading to enhancement in ionic conductivity. This semi-crystalline nature of PEO blends was also reported earlier for PEO-NaPF₆ solid-polymer electrolytes [9]. In this work, gel-polymer electrolyte samples were then prepared by incorporating six different weight percentages of PC to the optimized composition (PEO/Na⁺ = 10). PC, which is a liquid at room temperature, acts both as a solvent and the plasticizer and increases the amorphous nature of the polymer host leading to enhancement in room temperature conductivity (10⁻⁵ S cm⁻¹ for 75 wt% PC incorporation) (Fig.2). This conductivity value is two orders of magnitude lower than that of NaClO₄ and PC based liquid electrolytes. For example, Ponrouch *et al.*[12] reported room temperature conductivity value of 6 x10⁻³ S cm⁻¹ for a liquid electrolyte; 1M NaClO₄ dissolved in PC.

Incorporating nano-sized ceramic fillers such as TiO₂ is a well-known method to enhance the ionic conductivity in lithium-based solid-polymer electrolyte systems [5]. Here also, we tried to see whether TiO₂ gives similar enhancement in conductivity for this sodium-based system in the gel state. Different weight percentages of TiO₂ (2.5, 4, 5, 6, 7.5 and 10 wt%) nano-filler has been incorporated into the PEO-NaClO₄ (10:1) + 75 wt% PC gel-polymer electrolyte composition and the ionic conductivity values have been extracted from the impedance data. Although the conductivity enhancement is not that much significant compared to the filler free gel-polymer electrolyte mentioned above, NCGPE sample incorporated with 5 wt% TiO₂ showed the best enhancement (10⁻⁵ S cm⁻¹ at room temperature) as shown in Fig.2. In 2012, Chandra *et al.*[13] studied SiO₂ ceramic filler incorporated solid-polymer electrolytes based on PEO-NaPO₃. They also reported a conductivity enhancement due to the ceramic filler SiO₂ and the best conducting

composition was reported as 93[75PEO:25NaPO₃]:7 SiO₂ (wt%) with a room temperature conductivity of 2.5×10^{-6} S cm⁻¹. Compared to this, our best conducting NCGPE shows an order of magnitude higher room temperature conductivity, mainly because of its gel state.

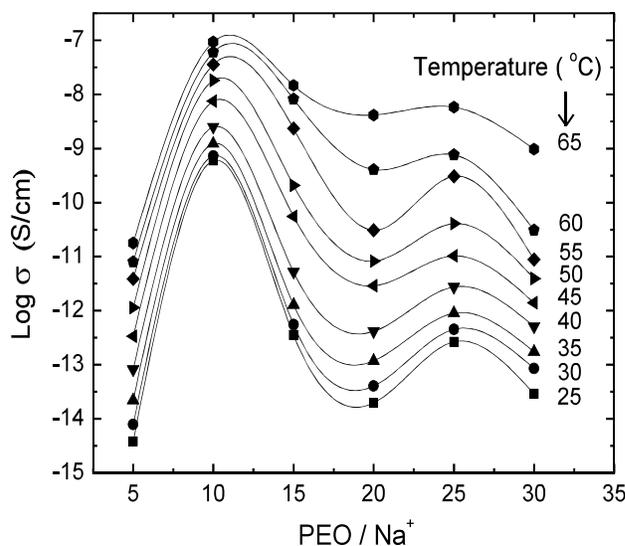


Fig.1. Conductivity variation for PEO-NaClO₄ solid-polymer electrolytes with PEO/Na⁺ molar ratio at nine different temperatures (25, 30, 35, 40, 45, 50, 55, 60 and 65 °C) .

TiO₂ has high Lewis-acid character [14] compared to other commonly used ceramic fillers such as Al₂O₃, SiO₂ and ZrO₂. Incorporation of TiO₂ may lead to high transient conducting pathways due to the Lewis acid-base type interactions between the polar surface groups of the filler and the ionic species in the electrolyte, as originally proposed by Wiczorek *et al.*[15] for lithium systems. Due to these Lewis-acid base interactions, there would be mainly two important structural modifications taking place at the ceramic surface [16-18]. One effect is the promotion of sodium-ion conducting pathways by lowering the PEO reorganization tendency through the cross-linking of PEO segments and anions on the polymer electrolyte. The other effect is the promotion of salt dissociation caused by the lowering of ionic coupling because of the Lewis-acid base interaction with the ionic species. In addition to this effect, TiO₂, due to its higher dielectric constant (435) compared to that of PEO (2.8-3.3) [5], would lead to active dissociation of Na salt resulting in an increased concentration of mobile carriers and thereby the conductivity. This active salt dissociation and the increased sodium-ion conducting pathways would lead to enhancement in ionic conductivity in these NCGPEs. When the TiO₂ content in the composite electrolyte is increased beyond 5 wt%, the effect of phase separation becomes increasingly dominant, resulting the blocking effect and subsequently an apparent reduction in conductivities.

DC polarization studies with SS blocking electrodes revealed that these electrolytes are predominantly ionic conductors showing very small electronic transference numbers; 0.08 for the sample without the filler and 0.17 for the sample with 5 wt% of TiO₂ filler. Fig.3 shows the DSC data taken during the heating cycle on the best conducting NCGPE (PEO₁₀ NaClO₄ + 75 wt% PC + 5 wt% TiO₂). This best conducting electrolyte showed a glass transition temperature (T_g) of -14.9 °C and a room temperature ionic conductivity (σ_{RT}) of 10⁻⁵ S cm⁻¹. Hopping of ionic species between the coordinating sites, better ionic dissociation due to the optimized PC and TiO₂ concentrations and the resulting increase in the segmental motion of the PEO polymer chains contribute to the optimum ionic conductivity. As explained by Yang *et al.*[8] for some other

sodium-ion conducting gel-polymer electrolyte systems, entrapment of liquid electrolyte within the pores of the polymer host and eventual swelling of the amorphous phase content would also help to enhance the ionic conductivity in our best conducting NCGPE

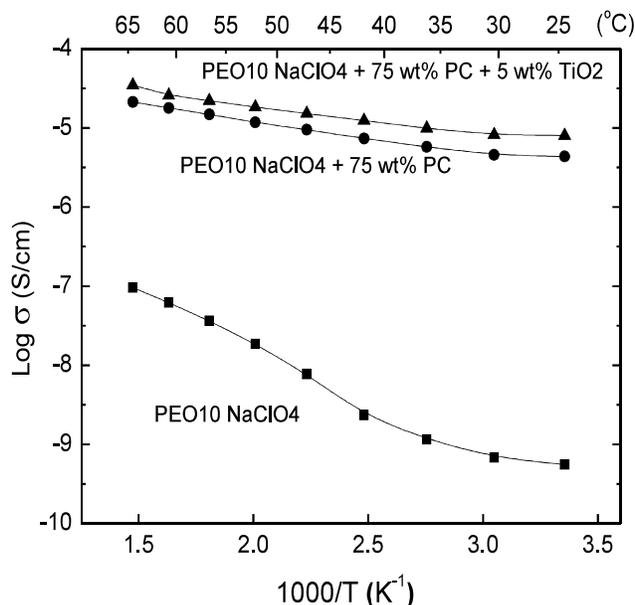


Fig.2. Conductivity variation with inverse temperature for PEO₁₀NaClO₄ (square), PEO₁₀NaClO₄ + 75 wt% PC (circle) and PEO₁₀NaClO₄ + 75 wt% PC + 5 wt% TiO₂ (triangle) polymer electrolytes.

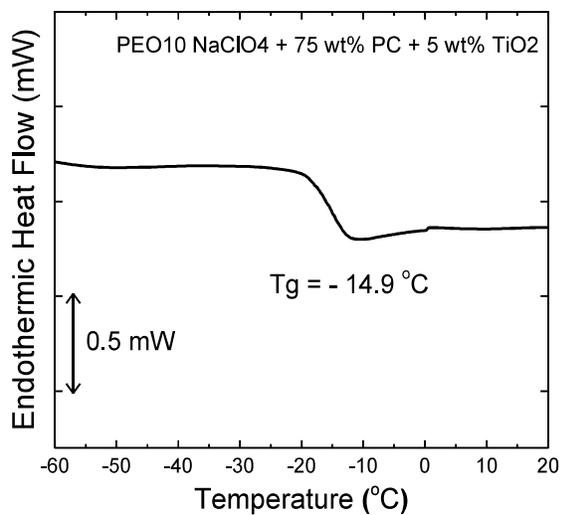


Fig.3. DSC thermogram taken during the heating scan with a scan rate of 20 °C/min on the best conducting NCGPE sample (PEO₁₀NaClO₄ + 75 wt% PC + 5 wt% TiO₂).

4. CONCLUSION

Three types of sodium-ion conducting polymer electrolytes have been studied in this work; solid-polymer (PEO₁₀NaClO₄), gel-polymer (PEO₁₀NaClO₄ + 75 wt% PC) and nano-composite gel-polymer (PEO₁₀NaClO₄ + 75 wt% PC + 5 wt% TiO₂) electrolytes. Optimized compositions in

these three different categories showed room temperature ionic conductivity values of 10^{-9} , 10^{-5} and 10^{-5} S cm⁻¹, respectively. Variation of ionic conductivity with inverse temperature showed Arrhenius behavior. The DC polarization analysis revealed that the electronic transference number (t_{elec}) of these electrolytes are very small, 0.17 for the best conducting NCGPE sample, confirming the dominant ionic conducting nature of these electrolytes. Thermal studies showed that the best conducting NCGPE has the glass transition temperature (T_g) of -14.9 °C.

5. ACKNOWLEDGEMENT

PR, KV and SS acknowledge National Research Council (NRC), Sri Lanka for the financial assistance (Grant #: NRC 15-078) to the project. KV also acknowledges University Research Grant (URG-2015) obtained from the University of Jaffna, Sri Lanka.

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