

PHYSICAL AND ELECTRICAL PROPERTIES OF Al₂O₃-PEO/PEG-BASED SOLID POLYMER ELECTROLYTE

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Abstract

This paper presents the investigation of physicochemical properties and ionic conductivity of PEO/PEG-based solid polymer electrolytes (SPEs). The SPEs were prepared by blending between poly (ethylene oxide) (PEO) and poly (ethylene glycol) (PEG). KI salt was added into the system of PEO blend PEG (PEO/PEG). The different amount of aluminum oxide (Al₂O₃) filler, 2-4 wt%, was loaded into the PEO/PEG/KI solid polymer electrolyte films. The lowest melting point and degree of crystallinity of the synthesized SPEs were observed on PEO/PEG/KI system with the addition of 2 wt% of Al₂O₃. The highest ionic conductivity of 8.64×10^{-7} S/cm was observed at 30°C for the incorporation of 4 wt% Al₂O₃. The activation energies of each region tend to decrease with the increasing concentration of Al₂O₃ filler.

Keywords: Solid polymer electrolyte, ionic conductivity, nanofiller, poly (ethylene oxide) (PEO), aluminum oxide

Introduction

Lithium-ion batteries (LIBs) are widely used in electric vehicles (EVs), automotive, and electronic devices (Yue *et al.*, 2016). LIBs are considered as most efficient for large-scale electrical power storage systems due to their advantages such as high voltage, high energy density, no memory effect, fast charging and long cycle life. Accordingly, LIBs are a promising technology to fulfill the requirements of next-generation EVs (Ding *et al.*, 2019). However, the energy density of the LIBs is relatively low compared to that of fossil fuels. Normally, the energy density of current LIBs is typically between 100 and 300 Wh/kg while the energy of gasoline is about 1,700 Wh/kg (Girishkumar *et al.*, 2010). Furthermore, LIBs are generally made from gel polymer and liquid/aqueous electrolytes those might

limit to operating temperature range, hermetically sealing, expansion, leakage, explosion, short circle life and safety problem (Chintapalli and Frech, 1996; Aram *et al.*, 2015).

Solid polymer electrolyte (SPE) is a revolutionary polymer electrolyte in solid-state ionic material. It exhibits outstanding high ionic conductivity at ambient temperature which is comparable to that of liquid/aqueous polymer electrolytes (Agrawal and Pandey, 2008). Poly(ethylene oxide) (PEO) is most widely used for SPEs because it shows a good electrical property such as solvating and transporting a number of lithium-ions (Choi *et al.*, 2000). However, the high crystallinity at a low temperature of PEO is the main drawback that limits its applications (Reddy, 2006). Moreover, the PEO

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electrolyte has less effective in dissociation of the lithium salt due to its low dielectric constant. This results in the formation of ion pairs or ion aggregates in the electrolyte system and a decrease in ionic conductivity (Nithita *et al.*, 2012; Ma *et al.*, 2016). The PEO chains allow the extension of helical conformation with repeat units compose of seven-O-CH₂-CH₂- groups in two turns of the helix. The chains can unfold around ions forming crown-ether-like multinuclear coordination complexes (Jatathilaka *et al.*, 2003). Thus, the crystalline derived from individual arranges wrapping chains forming lamellar crystals and eventually spherulites. The blending of PEO with poly (ethylene glycol) (PEG) not only facilitates the ionic conductivity but also improves the mechanical stability of SPEs (Mohamed *et al.*, 2013). PEG also leads to lower viscosity and decrease of crystallinity of PEO by interrupting intermolecular hydrogen bonding of PEO (Herzberger *et al.*, 2016). PEG is the plasticizer that promotes the amorphous phase content, increasing flexibility in the polymeric segments and dissociation of mobile charge carriers due to the ion dissolution effect.

The addition of inorganic fillers, especially nanoparticles, significantly reduces the degree of crystallization and also improves the stability of the electrode/ electrolyte interface, electrical property, mechanical stability and thermal stability (Nadimicheria *et al.*, 2015). The special functional group forming on the surface of the inorganic filler can form a hydrogen bond with the oxygen atom on the PEO segment. This will force the linear polymer chain deformation and results in reducing the crystallinity of the PEO polymer. As a result, the amorphous phase is developed that enhances the ionic transport properties. The fillers also act as a cross-linking center, interacting with both the polymer segment and the salts that will change the crystalline nature of the polymer segment and optimize the transport path for ions. It was reported that aluminum oxide (Al₂O₃) nanofiller and ethylene carbonate (EC) plasticizer were applied in PEO-LiCF₃SO₃ solid polymer electrolyte (Rajendran *et al.*, 2000; Nadimicheria *et al.*, 2015). The results indicated that Al₂O₃ nanofiller could enhance ionic conductivity with the decrease of crystallinity.

The present work is focused on the synthesis and the study of properties of PEO/PEG polymer electrolyte by the addition of Al₂O₃ to eliminate crystallinity and enhance ionic conductivity of the solid polymer electrolyte. Several experimental techniques such as scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and electrochemical impedance spectroscopy (EIS) were performed to characterize this polymer electrolyte.

Materials and Methods

Aluminium oxide nanoparticles were prepared by dissolving 8 ml of 5M of Al(NO₃)₃·9H₂O in 50 ml of a solution of 3.5 mM NaOH and 2 g of PEG-4000. The mixture was stirred thoroughly with nitrogen gas purging for 15 min. The solution was stored in the flask for 5 days at ambient temperature. White crystals were precipitated and assemble by centrifugation. The product was washed with distilled water and ethanol several times and dried in a vacuum at 50°C for 10 h. Finally, the product was calcinated at 850°C for 10 h.

Solid polymer electrolyte film was prepared by dissolving 3.5 g of PEO ($M_w = 600,000$), 1.0 g of PEG-4000 and 0.5 g of KI salt in 25 ml of methanol. The as-synthesized Al₂O₃ was added to the mixture at 2 or 4 wt%. The mixture was stirred thoroughly for 48 h at room temperature. The gel-like solution was cast on a silicone mold and allowed to slow evaporation in an oven under vacuum for 48 h. Finally, the dried solid polymer electrolyte film was peeled off from the mold and stored in a desiccator to avoid moisture and contamination.

The as-synthesized Al₂O₃ was examined by SEM model 1450 VP LEO. The thermal property of the SPE films was investigated by Differential scanning calorimetry (DSC) model 822e Mettler Toledo from -60°C to 100°C at a scanning rate of 10°C min⁻¹ under nitrogen atmosphere. The electrical conductivity of the SPEs was determined from the impedance measurement in the temperature range 30°C using E4990A impedance analyzer, IRC technologies in the frequency range of 20 Hz-1 MHz with a contact area of electrodes of 0.173 cm².

Results and Discussion

Figure 1(a) shows the SEM image of as-received Al₂O₃ particles. The primary particles with the size less than 1 μ m have been observed but they agglomerated to be secondary particles larger than 1 μ m. As a result, the Al₂O₃ particles are aggregate as quasi-sheet due to the absence of surfactant (Guo *et al.*, 2016). Figure 1(b) is the SEM image of Al₂O₃ powder blended with PEG-4000 and calcinated at 850°C. As a result, the addition of PEG-4000 can promote the de-agglomerated of primary particles. Therefore, the primary particles tend to separate on the substrate surface. From a previous study, PEGs acted as structure breakers and enhanced hydrophobicity those resulted in decreased interfacial adsorption and an increase in the critical micelle concentration (CMC) of Cetyltrimethyl

ammonium bromide (CTAB) (Manna and Panda, 2011).

The DSC curves of pure PEO, PEO/PEG/KI, and PEO/PEG/KI/Al₂O₃ are shown in Figure 2. The DSC thermographs for different SPE films have been investigated as the effect of incorporating potassium iodide (KI), plasticizer (PEG), and Al₂O₃ filler. The pure PEO shows an endothermic peak at about 65°C corresponding to the melting point of PEO. The melting transition temperature (T_m) decreased with the addition KI salt and plasticizer into the polymer matrix. The T_m was decreased to 58.0-59.0°C when PEG and KI were added into the system. The T_m is found to shift towards lower temperature for 2 wt%-addition Al₂O₃ filler into PEO/PEG/KI. However, the addition of Al₂O₃ filler at 4 wt% into PEO/PEG/KI SPEs tends to increase the T_m of the system. Similarly, a significant increase of T_m was also observed in PVA/PEO system with the addition of Al₂O₃ greater than 4 wt% (Joge *et al.*, 2013). This result is possibly due to the formation of the amorphous phase within the space charge layer.

The degree of crystallinity (χ_c) of SPEs shown in Table 1 is determined by Equation (1). using the values of the melting enthalpy of synthesized SPEs

(ΔH_m) and the melting enthalpy of 100% crystalline PEO ($\Delta H_{PEO} = 213.7$ J/g).

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_{PEO}} \times 100\% \quad (1)$$

From the DSC results, the melting enthalpy of PEO decreased from 186.5 to 99.1 J/g when PEG and KI were added which corresponding to the reduction of the degree of crystallinity from 87.3 to 46.4%. Adding Al₂O₃ to PEO-based electrolyte was also reduce the crystallinity. The result shows that adding 2 wt% of Al₂O₃ lowers the degree of crystallinity to 39.9% ($\Delta H_m = 85.3$ J/g). The results imply that the degree of crystallinity of PEO decreases due to the plasticizer, salt, as well as nanofiller. The addition of a plasticizer or filler also enhances the volume fraction of the amorphous phase (Joge *et al.*, 2013). However, adding more Al₂O₃ produce a contrary effect where the degree of crystallinity ascends to 49.8% when 4 wt% of Al₂O₃ was added. The higher amount of fillers might act as a nucleating agent and possibly cause the aggregation of Al₂O₃ particles (Zhu *et al.*, 2018).

Figure 3 shows the Nyquist plot of the fabricated SPEs measured at 30°C. Each Nyquist plot shows a semicircle in the high frequency region implying the properties of the electrolyte such as bulk resistance, R_b . As can be seen, the bulk resistance is approximated from the right-intercept of each semicircle line for a high internal resistance substance. Therefore, the resistance of the SPEs was 570 k Ω , 410 k Ω , and 130 k Ω for PEO/PEG/KI, PEO/PEG/KI+2wt% Al₂O₃ and PEO/PEG/KI+4

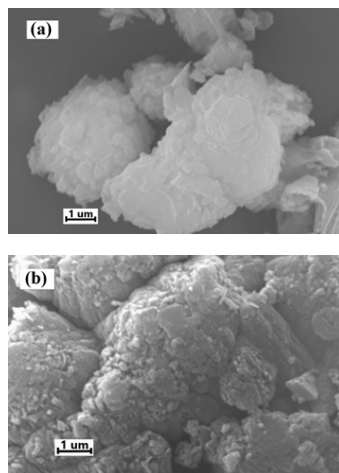


Figure 1. SEM images of (a) as-received Al₂O₃ particles (b) Al₂O₃/PEG-4000 calcinated at 850°C

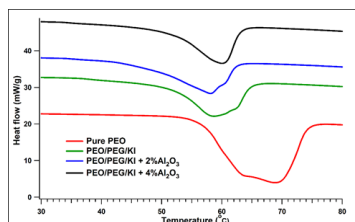


Figure 2. DSC curves of pure PEO, PEO/PEG/KI and PEO/PEG/KI with Al₂O₃

Table 1. Thermal property and degree of crystallinity of PEO/PEG-based polymer electrolytes

Samples	T_m (°C)	ΔH_m (J/g)	Degree of Crystallinity (%)
Pure PEO	65.0	186.5	87.3
PEO/PEG/KI	58.8	99.1	46.4
PEO/PEG/KI +2wt% Al ₂ O ₃	58.0	85.3	39.9
PEO/PEG/KI +4 wt% Al ₂ O ₃	60.1	106.5	49.8

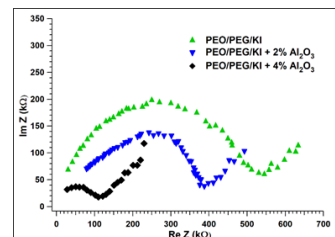


Figure 3. Nyquist plots of PEO/PEG/KI films with 0, 2 and 4 wt% of Al₂O₃ at 30

wt% Al₂O₃, respectively. The ionic conductivity has been calculated from the bulk resistance along with area (A) and thickness (t) of the sample as follows:

$$\sigma = \frac{t}{AR_b} \quad (2)$$

The conductivity of the SPE is shown in Table 2. It is obvious that the conductivity of SPEs varies nonlinearly with the amount of Al₂O₃. The enhancement in the ionic conductivity with the addition of Al₂O₃ may be due to the interaction of the filler particles with both the anion and cation (Croce *et al.*, 2001). According to the Lewis acid-base model, the Al₂O₃ filler enhances the ionic conductivity of SPEs by preventing the reorganization of the crystalline phase of PEO/PEG chains. The filler is able to penetrate the polymer matrix which promotes the interaction between plasticizer, ions, and polymer chain molecules. Consequently, the presence of various interactions in the polymer matrix between Lewis base centers on ether oxygen and the strong acid cation modifies the polymer chain structure which supports fast ionic transport. However, further increment of filler concentration results in a decrease in conductivity. This result is probably the restricted ionic and polymer segmental mobility caused by a large number of nanoparticles in a rigid matrix (Wang and Alexandridis, 2016).

The Arrhenius plots of logarithmic values of conductivity and temperature for PEO-PEG-based SPE have been shown in Figure 4. The change of conductivity with temperature is due to the segmental motion, which increases the free volume of the system. This increase in free volume would facilitate the movement of ionic charges (Aminah *et al.*, 2010). The plot of each composition results in the linear change of three regions i.e. (i) 304–320 K, (ii) 320–330 K, and (iii) 330–345 K. The regions (i) and (iii) might be the results of intrachain and interchain segmental motions, whilst the region (ii) may be due to the transition of the polymer from the crystalline to amorphous phase (Sasikala *et al.*, 2012).

The plot of $\log \sigma$ versus $1/T$ below 323 K temperature follows the Arrhenius behavior (Sunil *et al.*, 2015), expressed by

$$\log \sigma = \log \sigma_0 \exp \left(\frac{E_a}{kT} \right) \quad (3)$$

where σ_0 is the pre-exponential factor, T the absolute temperature, E_a the activation energy and k the Boltzmann constant. The activation energies were calculated from the slope of Arrhenius plots and the values are shown in Table 2. Those values vary from 0.30 eV to about 0.70 eV. The highest activation

energy of all samples can be determined from the region (ii) of Arrhenius plots. A similar result was reported for PEO+NaF electrolyte systems (Sasikala *et al.*, 2012). As can be seen, the activation energy tends to decrease with the increasing amount of Al₂O₃. Therefore, small amounts of dopant may form charge transfer complexes in the host lattice that increase the electrical conductivity by providing additional charges in the lattice, resulting in a decrease in activation energy (Mohan *et al.*, 2011).

Conclusions

The SPEs based on PEO-PEG-KI-Al₂O₃ complexes have been synthesized successfully by the solution casting method. The melting transition temperature and degree of crystallinity of pure PEO, PEO-PEG-KI are both decreased with the addition of 2 wt% Al₂O₃ filler. However, the values are increased for the addition of 4 wt% Al₂O₃ to the SPEs. The conductivity was found to increase with the increase in Al₂O₃ filler concentration. Therefore, the conductivities of the SPEs are 1.97×10^{-7} , 2.74×10^{-7} and 8.64×10^{-7} S/cm for PEO/PEG/KI, PEO/PEG/KI + 2wt% Al₂O₃ and PEO/PEG/KI + 4wt% Al₂O₃, respectively. The change of conductivity of the SPEs with temperature can be explained by Arrhenius behavior where the linear change is found in three regions. The activation energies of each region tend to decrease with the increasing concentration of Al₂O₃ filler.

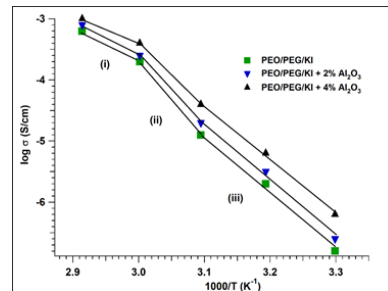


Figure 4. Arrhenius plot of the ionic conductivity for PEO-PEG-KI, PEO-PEG-KI+2 wt% Al₂O₃ and PEO-PEG-KI+4 wt% Al₂O₃ complexes

Table 2. Conductivity and activation energy of PEO/PEG-based polymer electrolytes

Samples	Conductivity, σ , at 30 °C (S/cm)	Activation energy, E_a (eV)		
		E_{a1}	E_{a2}	E_{a3}
PEO/PEG/KI	1.97×10^{-7}	0.32	0.73	0.52
PEO/PEG/KI + 2 wt% Al ₂ O ₃	2.74×10^{-7}	0.32	0.67	0.53
PEO/PEG/KI + 4 wt% Al ₂ O ₃	8.64×10^{-7}	0.26	0.61	0.50

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