

Effects of the Addition of LiCF_3SO_3 Salt on the Conductivity, Thermal and Mechanical Properties of PEO- LiCF_3SO_3 Solid Polymer Electrolyte

S. Klongkan and J. Pumchusak

Abstract—Solid polymer electrolyte for lithium ion batteries consisting of polyethylene oxide (PEO) and lithium trifluoromethanesulfonate (LiCF_3SO_3) was prepared by a ball milling method followed by a hot pressing process. Various contents of Li salts (5, 10, 15 and 20 wt %) were studied. The samples were investigated for crystallinity and glass transition temperature by DSC and ionic conductivity was measured by the impedance. XRD patterns confirmed the degree of crystallinity of solid polymer electrolyte. The mechanical property was measured by tensile testing machine. It was found that the PEO composite that composed of 15 wt% of LiCF_3SO_3 exhibited the highest conductivity at room temperature as $1.00 \times 10^{-6} \text{ Scm}^{-1}$, whereas the glass transition temperature (T_g), the melting temperature (T_m) and the degree of crystallinity decreased with the increasing of Li salt content.

Index Terms—Lithium salt, polyethylene oxide, solid polymer electrolyte.

I. INTRODUCTION

Lithium ion batteries are considered as talented systems not only for consumer electronics, such as electrochemical sensors, but also for electric vehicles. This is due to the high energy density and geometry flexibility of the polymer electrolyte [1].

Solid polymer electrolytes are a key element in energy storage or conversion devices that require high efficiency, high energy density, flexibility, and comfortable for assembly such as electrochemical capacitors, solar cells and lithium batteries. The advantages of solid polymer electrolytes such as no-leakage of electrolyte, flexible geometry, high energy density, good cyclability, good mechanical strength and safety have been the focus of many researchers to the development of new solid state electrolytes for replacing liquid electrolytes that may have inherent leakage, erosion, pollution, and packaging problems [2], [3].

Polyethylene oxide (PEO) has been extensively studied and the best candidates to be used as electrolyte and separator materials for lithium ion batteries in view of ionic conductivity and mechanical property [3]. PEO has been monitoring due to its stability, high ionic conductivity in the amorphous phase, high capacity in salt complexation, mechanical flexibility and corrosion resistance. The ion transport mechanism of this electrolyte is directly connected

to the alkaline salt (Li^+), creating coordination bonds [4], [5]. However, its low ionic conductivity at low room temperature causes the limitation of the device applications [6]. An important reason for the low ionic conductivity is that the presence of crystalline phase. It is usually the dominant phase in the PEO which hinders lithium ion transportation whereas high ionic conductivity is often associated with high temperatures amorphous phase [7]. Typically, several methods have been used to resolve these problems such as the addition of micro- or nano-scale fillers (Al_2O_3 , SiO_2 and TiO_2) [8], the addition of plasticizers (EC and PC) [5], [9], the implementation of uniaxial stresses, and the using of different kinds and volume of lithium salts. These conductivity enhancement methods are mainly aimed to reduce the crystallization of PEO, and so promote polymer ionic mobility. In addition, they give rise to the inhibition of crystallization, the decrease in glass transition temperature, the increase in the cation transport number, and hence the ionic conductivity is increased [2].

In this work, PEO- LiCF_3SO_3 was used to prepare the solid polymer electrolyte. The effect of different amounts of lithium salts on the conductivity, tensile properties and glass transition temperature of composites have been studied.

II. EXPERIMENTAL

A. Materials

Polyethylene oxide (PEO) powder (with an average molecular weight of 6×10^6 , Sigma-Aldrich) was used as a host polymer matrix. Lithium trifluoromethanesulfonate (LiCF_3SO_3 , Sigma-Aldrich) as the salt for complexation were vacuum dried for 24 h at 50 °C and 80 °C to remove the moisture before use.

B. Preparation of Solid Polymer Electrolytes

The PEO- LiCF_3SO_3 solid polymer electrolytes were prepared by a ball milling method followed by a hot pressing process. The percentages by weight of LiCF_3SO_3 were varied as 5, 10, 15 and 20.

The PEO and LiCF_3SO_3 powder was thoroughly mixed by ball-milling for 24 h to obtain a homogeneous mixture.

Hot pressing under a temperature of 135 °C and a pressure of 1800 psi was performed to form the composite membranes.

C. Materials Characterization

Differential scanning calorimetry was used to determine the melting temperature (T_m), glass transition temperature (T_g), recrystallized enthalpy (ΔH_m) and crystallinity (X_c) values of the solid polymer electrolyte by using a Mettler

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Toledo (DSC 1). The measurements were carried out in static nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ from -85 to 140°C in the heating cycle.

The X-ray diffraction (XRD) patterns of pure PEO and PEO-LiCF₃SO₃ solid polymer electrolyte were recorded using a Philips X' Pert MPD (Philips). The records were taken at room temperature using Cu K α radiation from 5 – 60° in the θ – 2θ scan with a scan rate 2°min^{-1} .

The ionic conductivity (σ) of polymer electrolyte was evaluated from complex impedance analysis using a LCR Hi-Tester (HIOKI-3520) in the frequency range of 1 Hz to 100 kHz at room temperature. The input voltage (V_{rms}) was 1 V . The ionic conductivity of the samples was measured by sandwiching between two stainless steel blocking electrodes. The ion conductivity was calculated from the expression in Equation (1).

$$\sigma = \frac{L}{RA} \quad (1)$$

where R is the resistance, L is the thickness of the electrolyte film and A represents the electrode area.

Tensile testing machine was used to determine the mechanical properties of the solid polymer electrolyte. The Lloyd universal testing machine (model LRX) with a rate of 1000 mm/min at room temperature was applied.

III. RESULTS AND DISCUSSION

A. Differential Scanning Calorimetry

The DSC of the pure PEO and solid polymer electrolyte are shown in Table I. The T_m , T_g and X_c values of the pure PEO (Fig. 1) are 62.79°C , -60.03°C and 60.21% , respectively. The addition of lithium salt into the system resulted the decrease of T_m , T_g and X_c in particular the 15% LiCF₃SO₃ (Fig. 2) gave the values of the T_m , T_g and X_c of 54.34°C , -64.37°C and 37.31% , respectively. This suggests that lithium salts contribute to the reduction of crystal phase.

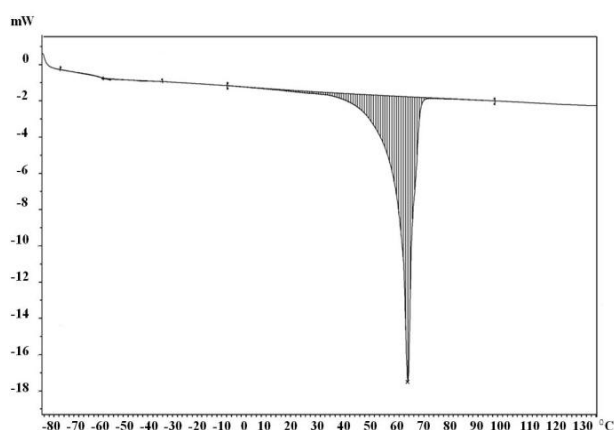


Fig. 1. DSC curves of pure PEO.

The T_g relates to the freezing of the movement of large molecules without changing in structure. Lower T_g usually leads to easier chain relaxation. In PEO-LiCF₃SO₃ solid polymer electrolytes, the T_g are lower when Lithium salt is added which shows that the segmental mobility of PEO in the composite increases upon the addition of lithium salt.

The reduction of T_m shows that the interaction between Lithium salt and the polymer matrix affects the main chain dynamics of the polymer. The PEO polymer is disturbed by lithium salt due to the coordination interactions between the Li⁺ ions and ether O atoms which causes the increase in amorphous nature of the polymer electrolytes as a result of a better ionic diffusivity and high ionic conductivity [10]. The relative percentage of crystallinity of PEO has been calculated using Equation (2).

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (2)$$

where ΔH_m is the experimentally melting enthalpy and ΔH_m^0 is a referenced melting enthalpy for 100% crystalline PEO (213.7 Jg^{-1}) [11]. The degree of crystallinity of solid polymer electrolyte decreases with the increase amount of lithium salt, which causes an increase in the amorphous phase. The polymer chain in the amorphous state is much more flexible than that of the crystalline state. This results the enhancement of the segmental motion of the polymer [12].

TABLE I: MELTING TEMPERATURE (T_m), GLASS TRANSITION TEMPERATURE (T_g), RECRYSTALLIZE ENTHALPY (ΔH_m) AND CRYSTALLINITY (X_c) VALUES OF PURE PEO AND PEO-LiCF₃SO₃ SOLID POLYMER ELECTROLYTE

Sample	T_m ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)	ΔH_m (Jg^{-1})	X_c (%)
Pure PEO	62.79	-60.03	128.68	60.21
PEO-5% LiCF ₃ SO ₃	62.89	-59.71	114.81	53.72
PEO-10% LiCF ₃ SO ₃	57.82	-61.81	93.28	43.65
PEO-15% LiCF ₃ SO ₃	54.34	-64.37	79.74	37.31
PEO 20% LiCF ₃ SO ₃	47.21	-65.98	51.90	24.29

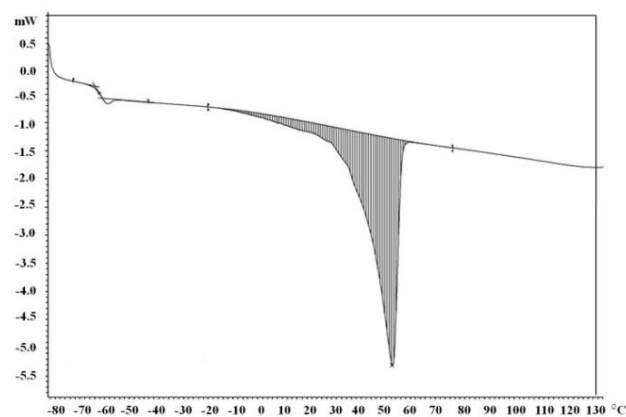


Fig. 2. DSC curves of PEO-15% LiCF₃SO₃ polymer electrolyte.

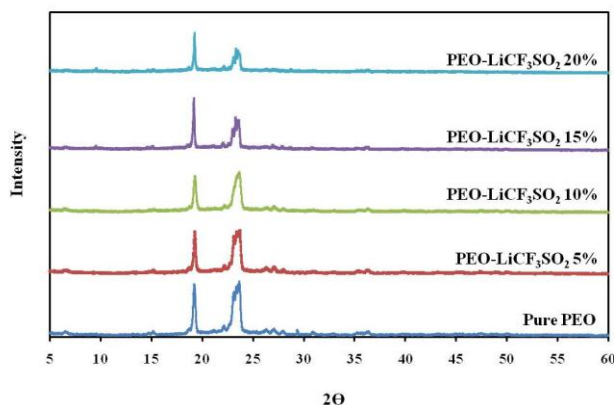


Fig. 3. XRD patterns of pure PEO and PEO-LiCF₃SO₃ polymer electrolyte.

B. X-ray Diffraction

The XRD patterns of pure PEO and PEO-LiCF₃SO₃ solid polymer electrolyte are shown in Fig. 3. The XRD of pure PEO contains two strong diffraction peaks at 19.19° and 23.63°. The higher intensity of these diffraction peaks is indicated that the PEO is crystalline polymer with high crystallinity [13]. However, the intensity of these peaks of crystalline PEO decreases after the addition of lithium salt into PEO. The decreasing is higher with the higher content of lithium salt. The reduction in crystallinity of the polymer electrolyte has been confirmed by DSC results, which were discussed above.

C. Ionic Conductivity

The ion conductivity of pure PEO and polymer composite electrolyte at various wt% of LiCF₃SO₃ salts (5, 10, 15 and 20 wt.%) are shown in Table II. The ion conductivity of pure PEO is 1.53×10^{-7} S cm⁻¹. When adding lithium salt into the system, the ion conductivity increased. Fig. 4 shows the highest conductivity of PEO-LiCF₃SO₃ system at 15 wt% of LiCF₃SO₃, which is 1.00×10^{-6} S/cm⁻¹ at room temperature and then decreases with further increase of salt concentration.

The ion conductivity increases upon the addition of salt could be explained by the decrease of the degree of crystallinity and also the increase in charge carriers as the number of free cation increases [14].

TABLE II: IONIC CONDUCTIVITY OF PURE PEO AND PEO- LiCF₃SO₃ POLYMER ELECTROLYTE

Sample	Conductivity (S cm ⁻¹)
Pure PEO	1.53×10^{-7}
PEO-5% LiCF ₃ SO ₃	2.00×10^{-7}
PEO-10% LiCF ₃ SO ₃	2.54×10^{-7}
PEO-15% LiCF ₃ SO ₃	1.00×10^{-6}
PEO-20% LiCF ₃ SO ₃	6.23×10^{-7}

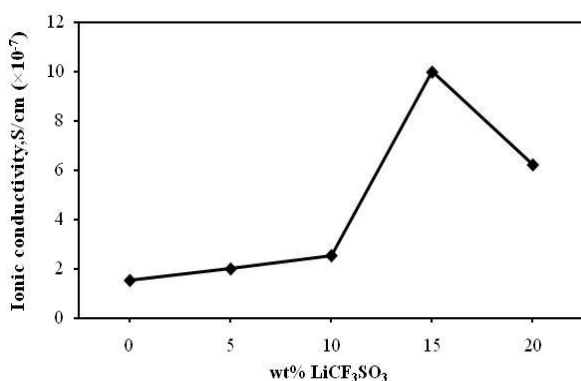


Fig. 4. Conductivity of PEO and PEO composites with different wt% of LiCF₃SO₃.

In the PEO-20 wt% LiCF₃SO₃ membrane, the ion conductivity decreased as compared to 15 wt% LiCF₃SO₃. It was explained by Ramesh *et al.* [15] that this could cause by the appearance of water molecules. It is known that, the LiCF₃SO₃ has a very strong ability to absorb water molecules. So, at 20 wt% of LiCF₃SO₃ in PEO, more moisture was being absorbed and the mobility of PEO-LiCF₃SO₃ system increased. As a result, water molecules form hydrogen bonding with PEO and hindered the linkage forming between PEO-LiCF₃SO₃ systems [15].

D. Mechanical Properties

Tensile tests were performed on the membrane of pure PEO and PEO-LiCF₃SO₃ polymer composite electrolytes and the results are shown in Fig. 5. The pure PEO membrane had the stress at maximum load, the percentage strain at maximum load and Young's modulus of 22.2 MPa, 3520 % and 205.0 MPa, respectively as shown in Table III. The addition of lithium salt into the PEO matrix caused the reduction of mechanical properties (Fig. 5), in particular, the stress at maximum load and Young's modulus of PEO-15% LiCF₃SO₃ composite are extremely lower than that of pure PEO. The PEO-15% LiCF₃SO₃ polymer electrolyte had the stress at maximum load, percentage strain at maximum load and Young's modulus of 5.4 MPa, 3225 and 12.8 MPa, respectively.

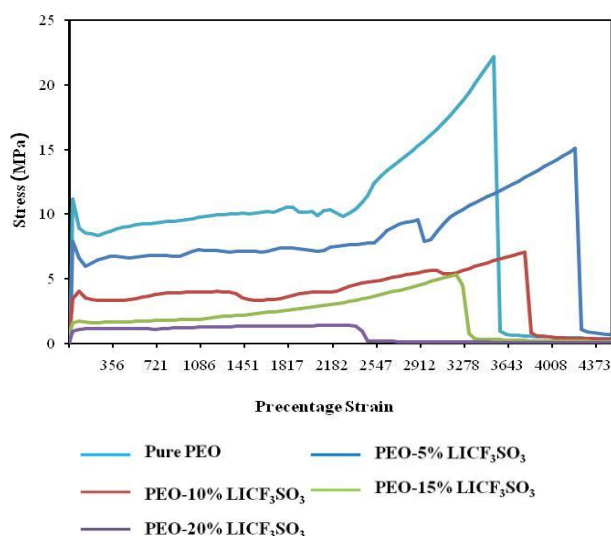


Fig. 5. Tensile stress-strain behavior of pure PEO and PEO-LiCF₃SO₃ polymer electrolyte.

TABLE III: MECHANICAL PROPERTIES OF PURE PEO AND PEO-LiCF₃SO₃ POLYMER COMPOSITE ELECTROLYTE

Sample	Stress at Maximum load (MPa)	Percentage Strain at Maximum Load	Young's Modulus (MPa)
Pure PEO	22.2	3520	205.0
PEO-5% LiCF ₃ SO ₃	15.1	4199	132.0
PEO-10% LiCF ₃ SO ₃	7.1	3796	39.8
PEO-15% LiCF ₃ SO ₃	5.4	3225	12.8
PEO-20% LiCF ₃ SO ₃	1.4	2298	4.7

This could be due to the involving of lithium salt in the inhibition of the crystallization, causes the increase of amorphous phase. As a result, the strength of the polymer electrolyte decreased. In addition, lithium salt particles may obstruct the passing of the polymer chains as the percentage strain also decreased. This is consistent with the research of Ji *et al.* [16] that has proved that in PEO based polymer electrolytes systems, the mechanical properties of composites would decrease as the salt concentration increased.

IV. CONCLUSION

PEO-LiCF₃SO₃ solid polymer electrolytes have been prepared via a ball milling method followed by a hot pressing process. The effects of lithium salts on the composites have

been evaluated from their mechanical properties, thermal characteristics and ion conductivity. The DSC analysis revealed a decrease in the T_m , T_g and X_c of PEO with the addition of lithium salt into the system. The degree of crystallinity in pure PEO and PEO-LiCF₃SO₃ polymer electrolyte system has been confirmed by the XRD and the DSC results. The ionic conductivity at room temperature is increased with the increased of the amount of LiCF₃SO₃ salt. It was found that in PEO-LiCF₃SO₃ system, 15wt % LiCF₃SO₃ in PEO has the highest ion conductivity as $1.00 \times 10^{-6} \text{ S cm}^{-1}$. The stress at maximum load, percentage strain at maximum load and Young's modulus of the PEO-15% LiCF₃SO₃ polymer electrolyte are 5.4 MPa, 3225 and 12.8 MPa, respectively. This suggests that the PEO-15% LiCF₃SO₃ polymer electrolyte is a feasible candidate electrolyte membrane for all-solid-state lithium ion batteries.

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