

Enhancement of the Conductivity of the Polymer Electrolyte by Nano Al₂O₃

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Abstract: Polymer electrolyte was prepared by using PMMA –LiBr by solution casting method. The nano Al₂O₃ plays an important role to enhance the conductivity of PMMA –LiBr polymer electrolyte. The ionic conductivity of the polymer electrolyte was measured by impedance spectroscopic technique. The highest room temperature conductivity of the electrolyte of the electrolyte of $1.65479 \times 10^{-7} \text{Scm}^{-1}$ was obtained at 2.5 % by weight of Al₂O₃. The conductivity of the electrolyte increases with the percentage weight of the nanomaterial. The prepared samples were studied using FTIR, XRD and SEM.

Keywords: ionic conductivity, PMMA (Polymethylmethacrylate), polymer electrolyte, inorganic filler, surface morphology, Nanocomposite polymer electrolyte.

1. INTRODUCTION

During the past decade, considerable effort has been devoted to the development of solid polymer electrolytes with high ionic conductivity at room temperature [1]. Addition of fillers to salt doped polymer electrolyte has been the subject of much interest because of large increase in conductivity, higher cationic transport number and increase electrochemical stability due to their incorporation in polymer matrices [2]. The role of filler in a solid polymeric electrolyte system is crucial as it serve as an agent to improve the conductivity of the electrolyte. There are two types of filler that can be introduced in the electrolyte system, namely, organic and inorganic molecule filler. The disadvantage of organic molecule filler such as propylene carbonate (PC) and ethylene carbonate (EC) is that they are more expansive compared with inorganic molecule filler [3]. The solid polymeric electrolyte of PMMA - LiBr with the organic molecules filler of propylene carbonate (PC) has been used in photo electrochemical cells of TiO₂ /PMMA-LiBr/graphite as the medium for the redox reaction to take place [4]. However the cells performance is poor due to the low conductivity of the electrolyte.

Improving the conductivity of the electrolyte is to introduce inorganic compound filler and plasticizer replacing the costly organic molecules filler such as SiO₂, TiO₂, SnO₂, Al₂O₃, DMF (Dimethyl formamide) into the polymeric electrolyte system [5-10]. This filler promotes

more free lithium ions and produces more amorphous regions in the electrolyte for charge carriers to transfer. Therefore, the conductivity of the electrolyte could be improved.

In this work, we prepared a solid polymeric electrolyte of PMMA - Al₂O₃ - LiBr with Al₂O₃ as filler. Al₂O₃ filler was chosen as it is a cheaper material than PC filler. The objective of this work is to study the effect of amount of Al₂O₃ on the ionic conductivity, thermal behavior and morphology studies of PMMA-LiBr solid polymer electrolyte [3].

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

0.75gram of PMMA (60,000 mw) was dissolved into 20ml THF (Tetrahydrofuran) and stirred using a magnetic stirrer to form a homogenous solution. 0.25 gram of LiBr was then added in to the solution. 0.02 gram of Al₂O₃ was then added into the solution and the mixture were then stirred for 24 hours and then poured into a Petri dish and left for slow drying to room temperature to form a electrolyte films. The dried films were obtained after THF solvent has completely evaporated. The films were then peeled off from the dish. These steps were repeated for preparing PMMA - Al₂O₃ - LiBr with 2.5wt%, 5.0 wt%, 7.5wt% and 10.0wt% of Al₂O₃. The films with thickness of 0.07 – 0.1 mm were kept in desiccators for further use. The samples were further dried in a vacuum oven. The objective of this work is to study the effect of amount of Al₂O₃ on the ionic conductivity, FTIR analysis, XRD and surface morphology (SEM) of PMMA- LiBr solid polymer electrolyte.

3. RESULT AND DISCUSSION

3.1. Ionic conductivity

The ionic conductivity is calculated using the equation

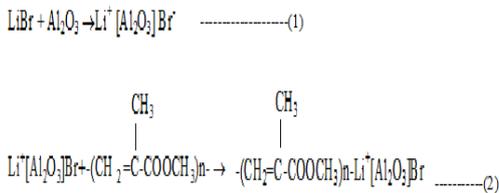
$$\sigma = l / (R_B A),$$

Where l is the thickness of the polymer electrolyte film, A is the surface area of the film and R_B is the bulk electrical resistance value [11]. The ionic conductivity of

the polymer electrolyte depends on the effective number of carrier ions and the ions mobility. The effective number of carrier ions is related to the concentration of the dissolved ions. The ion mobility in a polymer electrolyte formed by the dissolution of ions in the polymer is facilitated by the segment mobility of the polymer chains [12].

An increasing of ionic conductivity with Al₂O₃ content is attributed to a reduction of crystallinity of composite polymer electrolyte. A reduction of crystallinity arises from random distribution of fine Al₂O₃ powder which may introduce the topological disorder in the electrolyte. A polymer chain in the amorphous phase is more flexible, which result in an increasing of segmental motion of the polymer. Another factor enhancing the electrolyte conductivity is presence of the oxygen concentration in the Al₂O₃ filler. The oxygen group may prevent Al₂O₃ atoms from contacting with the polymer electrolyte so that the interaction between Al₂O₃ and PMMA - LiBr are stronger, leading to higher conductivity of the electrolyte [10]. The presence of Al₂O₃ could result in a great number of charge carriers for ionic transport [5]. The cation Li⁺ transports is similar as free volume model, where cation is transferred to the coordinating sites in the same polymer chain or to the neighboring polymer chain. The segmental motions of the chain promote the cation transport and hence increase the ionic conductivity [13].

The ion dissociation in PMMA - Al₂O₃ - LiBr composite polymer electrolyte. The reaction is mentioned in Scheme-1.



Scheme-1

Table.1 shows the relationship between the conductivity of PMMA - Al₂O₃ - LiBr electrolyte and Al₂O₃ concentrations at room temperature. It was observed that the conductivity varies with the concentration of Al₂O₃ filler. The conductivity increases from 2.5 wt% to 10wt% Al₂O₃. From the table1, the lowest conductivity is 1.142×10⁻⁸ S cm⁻¹ obtained at 10 wt% of Al₂O₃ and the highest value is 1.65479×10⁻⁷ Scm⁻¹ obtained at 2.5% of Al₂O₃. The introduction of inorganic filler into the electrolyte system will make the electrolyte be more amorphous and promotes more free lithium ions from the inorganic salt of LiBr to transfer in the electrolyte [5].

TABLE.1. Ionic conductivity of PMMA - Al₂O₃ - LiBr.

Weight % of Al ₂ O ₃	Thickness l (cm)	Resistance R _B (ohm)	Ionic conductivity σ (Scm ⁻¹)
2.5	0.0079	2.8×10 ⁴	1.65479×10 ⁻⁷
5	0.0101	3.8×10 ⁴	1.55888×10 ⁻⁷
7.5	0.0125	1.4×10 ⁵	5.23669×10 ⁻⁸
10	0.0076	3.9×10 ⁵	1.14294×10 ⁻⁸

Thus, in this research, it was continued only up to 10wt% of Al₂O₃ in polymer matrices although ionic conductivity increases with increases amount of filler. The higher filler concentrations, the grains get close to each other that the blocking effect improved by the more abundant alumina grains could make the long polymer chains more “immobilized” leading to the decreasing conductivity [19].

3.2. FTIR analysis

PMMA has ester functional groups (COOCH₃) in the side chain. These groups can interact with the other functional group. PMMA shows a peak at 1728cm⁻¹ which corresponds to C=O (free carbonyl group). The combinational bands at 3622cm⁻¹, 3545cm⁻¹ and 3435cm⁻¹ are assigned to the vibrations of CH₂ groups. Two distinct bands appeared at 2993 cm⁻¹ and 2951 cm⁻¹. The first band arises from the asymmetrical stretching mode in which two C-H bonds of the methyl group are extending, while the third one is contracting and the second band arises from CH₃ symmetrical stretching in which all three of the C-H bands extend and contract in phase[16]. As seen in figure.1 the vibrations CH₂ stretching, CH₃ bending, symmetrical CH₃ bending are observed at 1481cm⁻¹, 1437cm⁻¹ and 1386cm⁻¹ respectively. The vibrations C-O-O ending and C-H out of plane bending are observer at 840cm⁻¹ and 752cm⁻¹ respectively [17, 18]. When LiBr is added with PMMA, the intensity of the peak corresponding to the reacting functional group C=O decreases and get shifted from 1728cm⁻¹ to 1699cm⁻¹ as a broad peak. The combinational band for CH₂ group vibrations 3622cm⁻¹, 3545 cm⁻¹, 3435cm⁻¹ have found to disappear in the PMMA+LiBr system. The band for CH₂ stretching 1481cm⁻¹ is also changed. It can be seen from figure.1b that the vibrational band at 1437cm⁻¹ of pure PMMA has been shifted to 1433 cm⁻¹ due to the addition of LiBr. The CH₃ and C-H vibrational bands 1386cm⁻¹ and 840cm⁻¹ of pure PMMA have been shifted to 1388cm⁻¹ and 842cm⁻¹ respectively. The observed shifts of vibration bands, the disappearance of bands and change in the intensity and width of peaks proved that there is a complex formation between PMMA and LiBr.

PMMA - Al₂O₃ - LiBr system: The FTIR for this system is given in figure.1a. The C=O stretching band 1699cm⁻¹ of PMMA-LiBr complex is shifted to 1724cm⁻¹ in PMMA - Al₂O₃ - LiBr. The CH₃ symmetrical bending mode of PMMA-LiBr 1388cm⁻¹ is shifted to 1386cm⁻¹ due to the addition of Al₂O₃ filler. The band at low frequency

region of PMMA suffered intensity reduction and broadening due to the addition of LiBr to PMMA.

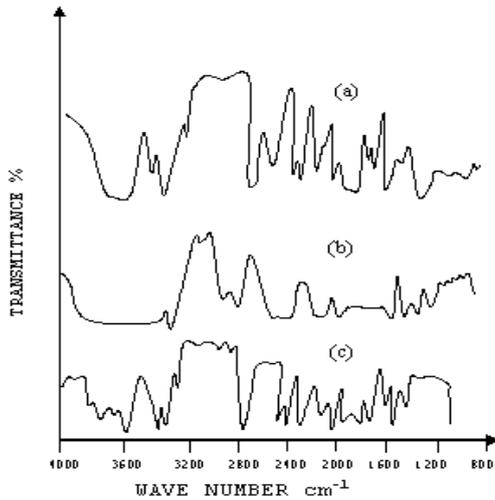


Figure 1. FTIR spectrum of

- (a) PMMA-LiBr-Al₂O₃ (2.5%)
- (b) PMMA-LiBr
- (c) Pure PMMA

The O-CH₃ stretching 1240cm⁻¹ of PMMA is disappeared in PMMA-LiBr. The addition of Al₂O₃ to PMMA-LiBr has led to a gain of intensity of the same vibration. These observations have indicated that Al₂O₃ has promoted the molecular vibrations in the complex.

3.3. SEM analysis

Figure 2 and 3 shows the scanning electron microscope micrograph of polymer electrolyte films surface morphology with and without Al₂O₃ contents respectively. With the presence of Al₂O₃ filler, the film surface becomes rough with some small aggregates. The Al₂O₃ particles are well distributed in the entire surface region [7]. It can be clearly seen from figure 3, the Al₂O₃ particle fill in the pores between the polymer matrices. The micro aggregates of in the pores will give a compensating effect on the transport property of Li⁺ ions, hence improving the conductivity of the electrolyte [7]. Thus ionic conductivity of PMMA based polymer electrolyte increases with increases weight of Al₂O₃. However, at higher concentration of Al₂O₃, it tends to agglomerates and size of the particles appears large. Even though this system gives the highest conductivity but this conductivity value is still low and not significantly implemented especially for ionic and electrochemical devices [14]. This low ionic conductivity is measured up to 0.1 gram Al₂O₃ in polymer matrices.

Further addition of alumina filler in the solid polymer electrolyte system may saturate the system due to the agglomeration of Al₂O₃ particle. Thus, caused the ions

to congest in the system and reducing the segmental motion in polymer chain.

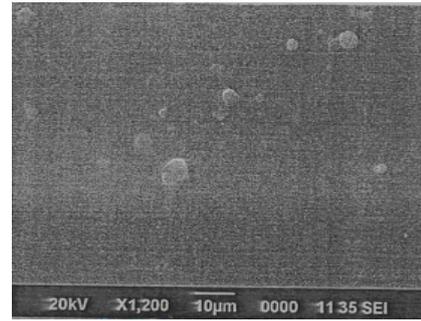


Figure 2. SEM image of PMMA-LiBr

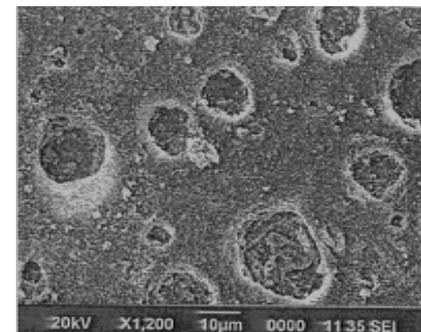


Figure 3. SEM image of PMMA-LiBr-Al₂O₃ (2.5%)

Therefore, the number of charge carrier will reduce and decrease the ion mobility and as a result, the rate of ionic conductivity of the system reduced [15].

3.4. XRD Analysis

The XRD patterns are taken for the PMMA-LiBr complex and the nanocomposite polymer electrolyte films for which the conductivity has showed the enhancement. The XRD patterns are given in figure.4.

A peak with maximum intensity is observed at 2θ around 12° and less intense peaks are observed at 2θ around 30°, 45° and 60° for PMMA-LiBr complex. The observed Bragg's peak at 12° is retained for the filler added complexes but with a significant decrease in peak height and broadening. This may be attributed to the reduction in crystallinity and increase of amorphous nature due to the addition of the filler [20].

The amorphous characteristic of the nanocomposite polymer electrolyte (NCPE) film produces much higher ionic transport. This is due to more flexible local chain segmental motion in the NCPE system [21]. The effect of chain mobility on ionic conductivity could be generally correlated with the free volume of the polymer. As the free volume within the polymer increases, rotation of the polymer chain occurs more rapidly and ion transport in polymer electrolyte is more rapid [22].

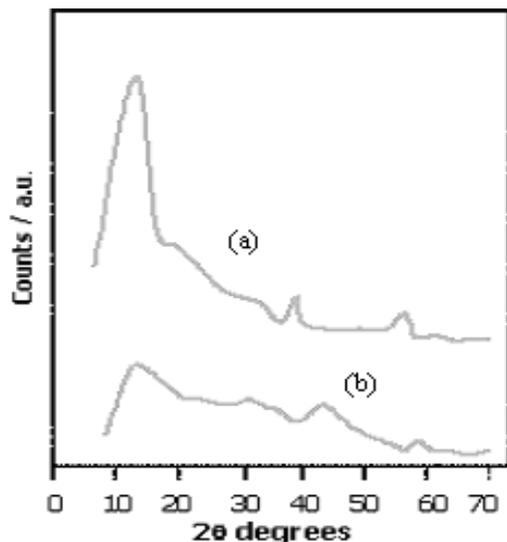


Figure 4. XRD pattern of polymer electrolytes

- (a) PMMA + LiBr
 (b) PMMA + LiBr + Al₂O₃ (2.5wt %)

Thus, the purpose of adding filler is to increase the amorphous nature, which in turn increases the free volume of the polymer electrolytes resulting in an increase in ionic conductivity.

4. CONCLUSIONS

In this paper, we have successfully prepared the solid polymeric electrolyte of PMMA - Al₂O₃ - LiBr where Al₂O₃ as filler to replace a costly organic filler. The result shows that the conductivity of the electrolyte is affected by the concentration of filler. The highest conductivity of the electrolyte of $1.65479 \times 10^{-7} \text{ Scm}^{-1}$ was obtained at 2.5 wt% of Al₂O₃. Further research is to be carried out in order to improve the conductivity of the solid polymeric electrolyte of PMMA - Al₂O₃ - LiBr to make it suitable for solid polymer electrolyte for Dye sensitized solar cell (DSSC) application.

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