Structure, thermal and electrical properties of PVDF-HFP/LiBOB solid polymer electrolyte

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Abstract. Solid polymer electrolyte (SPE), which is composed of poly (vinylidene fluororide-co-hexafluoropropylene) (PVDF-HFP), lithium bis(oxalate) borate (LiBOB) salt and various concentrations of TiO2 as filler, has been prepared by solution casting technique. Structure, thermal and electrical properties of the SPE were examined using XRD and SEM, TG/DSC, and impedance spectroscopy, respectively. XRD analysis reveals amorphous nature of PVDF-HFP/ LiBOB and TiO2 composite matrix. SEM photographs of polymer electrolyte membrane indicate good compatibility between polymer, salt, and other contents as well as amorphous phase formation in the fabricate of SPE. We obtained that (SPE) with composition of 70 wt% polymer, 28 wt% LiBOB and 2 wt% TiO2 has highest conductivity. XRD and DSC analysis indicate that the conductivity increases due to high amount of amorphous nature content. We suggest that the amorphous nature content may enhance segmental flexibility of polymeric chains and disordered structure of the electrolyte.

1. Introduction

Research on SPE is very interesting because it has a very wide range of applications in electrochemical devices such as rechargeable batteries, cell phone batteries, capacitors, fuel cells, memory devices, sensors, electrochromic devices, etc. [1]. SPE has many advantages, such as solvent free conditions, safe and light. It also has high specific energy, wide electrochemical stability windows, and easy to make. However, research on solid polymer electrolyte is still challenging as it has low ionic conductivity [2]. Polymer electrolyte membranes have been used effectively to replace liquid electrolytes. Studies have shown that polymer electrolyte membranes can reduce leakage in electrical devices that often occur in liquid electrolyte systems [3].

The presence of ionic conductivity is due to movement of the conduction species provided by inorganic salts dissociating into ions. Ions in the membrane move primarily through the solvent that contributes to the increase in conductivity [4]. Solid polymer electrolyte can be used as both the separator to avoid the electrode electrolyte contact and used as ionic conductor in matter of secondary rechargeable batteries. Usually polymer electrolytes of high molecular weight salt with compatible concentration can be used as a membrane which permits formation of anions and cations by dissociation of the salt. The increase of ionic conductivity due to an increase of mobility of cations [1]. Lithium bis (oxalate) borate (LiBOB) is one of new lithium salts applied to lithium ion battery (LIB). LiBOB has better thermal stability and higher capacity retention compared to electrolyte (LiPF6), but it has lower ionic conductivity [5].

Synthesizing solid polymer electrolytes by fillers is to inhibit the crystalline. An addition of filler can speed up segmental polymer dynamics and then create a greater ion transfer leading to a further
improvement of the conductivity. Integration of inorganic filler such as TiO$_2$, ZrO$_2$, Al$_2$O$_3$, SiO$_2$, SnO$_2$ and V$_2$O$_5$ into solid polymer electrolyte can increase conductivity, electrochemical stability, mechanical stability, cation transference number and thermal stability towards electrode materials. Otherwise, high dielectric constant of fillers may reduce interfacial resistance [6, 7].

Several polymers can be used in the synthesis of polymer electrolyte such as poly (ethylene oxide) (PEO), polyacrylonitrile (PAN), poly(vinylchloride) (PVC), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and poly (methyl ethacrylate) (PMMA) [8-12]. PVDF-HFP has more flexibility, a high dielectric constant (8.4) and a low glass transition temperature. VDF in PVDF-HFP polymer is crystalline nature that has chemical stability and HFP is amorphous nature. Crystalline nature of PVDF, and amorphous nature of HFP may give mechanical stability and an increase in ionic conductivity. Moreover, strong electrons with functional groups (-C-F) in PVDF-HFP make the polymer highly anodically stable [1].

Solid polymer electrolyte based on PVDF-HFP – LiBOB is also contributed by (TiO$_2$), ZrO$_2$, and Al$_2$O$_3$ [11, 14-17]. This paper explains structure, thermal and electrical properties of PVDF-HFP/LiBOB salt and TiO$_2$ as polymer electrolyte membrane. The electrolyte salt used in this research is LiBOB salt from synthesis using PA material [15]. Characterization of crystal structure and morphology were carried out using XRD and SEM, respectively. Thermal and electrical properties were analysed using TG/DSC and impedance spectroscopy. DSC study reveals the thermal properties of the polymer i.e. melting point, melting enthalpy and relative percentage of crisstalinity of the polymer electrolyte system.

2. Experimental Methods
2.1. Material

Material used for manufacturing of solid polymers elektrolit (SPE) were poly(vinylidenefluoride) - hydro furan phosphate (PVDF-HFP) as polymer (Sigma Aldrich), lithium bis(oxalate) borate (LiBOB) synthesized with PA material as lithium salts, titanium oxide (TiO$_2$) as ceramic filler (Merck), and N,N-dimethylacetamide (DMAC) from Merck Milliopore, Germany was directly used as a solvent. All the materials used are not purified.

2.2. Preparation

Solid polymer electrolyte (SPE) was prepared by solution casting technique. Amounts of PVDF-HFP polymer 70 wt% with different concentrations of LiBOB salt (30, 28 and 25 wt%) and addition of TiO$_2$ of 2 wt%, 5 wt% and without addition of TiO$_2$ were dissolved in N,N-dimethylacetamide (DMAC). Mixing process was carried out on hot plate and mixed by magnetic stirrer until the solution becomes homogeneous. Polymer, salt, and filler solution (slurry) were then poured / casted on a board / glass substrate and then allowed to dry at room temperature conditions. Sample drying process is carried out naturally at room temperature for ± 48 hours and then the polymer membranes were stored in the desiccators or dry box for further use and analysis.

2.3. Sample Characterization

XRD patterns of solid polymer electrolyte (SPE) samples were observed using X-ray diffraction (XRD) Rigaku type Smartlab under Cu Kα radiation within 2θ range of 10°- 60°. Morphology was studied using SEM (Jeol JED 350). Thermal properties was studied using TG/DSC (Linseis) at heating rate of 10°C min$^{-1}$ and the analysis was carried out at the first heating of 0 - 240°C. The electrical properties were studied using impedance spectroscopy. Ionic conductivity was studied by electrochemical impedance spectroscopy (EIS) method using LCR meter and HOIKI 3532150 chemical impedance meters. Variations of the samples carried out in this study are presented in table1.
Table 1. Sample composition for solid polymer electrolyte (SPE).

| Sample | PVDF HFP (wt%) | LiBOB synthesized with PA material (wt%) | TiO₂ filler (wt%) |
|--------|----------------|------------------------------------------|------------------|
| 1      | 70             | 0                                        | 0                |
| 2      | 70             | 0                                        | 30               |
| A1     | 70             | 30                                       | 0                |
| A2     | 70             | 28                                       | 2                |
| A3     | 70             | 25                                       | 5                |

3. Results and Discussion

3.1. X-ray diffraction Analysis

Presence of a sharp peak in X-ray diffraction analysis provides information on sample nature, crystal structure, crystal orientation, crystal size, crystallinity, amorphous and phase change of materials. Amorphous material (non-crystalline sample) is analyzed by one or two broad humps or peaks. Hodge et al. (1996) observed the correlation between intensity of X-ray diffraction and degree of crystallinity. In SPE, intensity of X-ray diffraction decreases indicating an increase of amorphous nature [20]. Amorphous nature in the polymer will support the conductivity properties of the sample [18]. X-ray diffraction patterns are obtained at room temperature for SPE of PVDF-HFP-LiBOB, PVDF- HFP – TiO₂ and PVDF – HFP-LiBOB with various wt% of TiO₂ are shown in figure 1. X-ray diffraction peaks of the PVDF-HFP membrane observed at 2θ = 20.4° and 38° shows the characteristics of semi-crystalline microstructure, e.g. the co-existence of mixed crystalline and amorphous regions [12].

In figure 1, A1 shows that an addition of LiBOB salt will cause new peaks appear at 14.7°, 25.2°, 28°, 29°, 31.2°, 36.8° and 37.7°, which may explain the complexation of LiBOB salt with the polymer PVDF – HFP. This indication may also show amorphous nature of the salt – polymer matrix. An addition of TiO₂ by 2% and a decrease in LiBOB concentration cause decrease of peaks intensity at 2θ = 14.7°, 20.1°, 25.22° and 36.8°. However, at 2θ = 28°, the intensity of the peak increases as shown in figure 1 for A2. These phenomena show that there has been an interaction / incorporation of TiO₂ fillers into the polymer-salt system. These also indicate amorphous nature and decreasing of the crystallinity of the salt – polymer matrix. In figure 1, A3 shows an increase of TiO₂ concentration and a decrease of the LiBOB salt concentration. At 2θ = 14.74°, 20.22°, 36.7° and 37.7°, we observe increase of peak intensity that may be caused by an increase in the crystallinity. The segmental relaxation of the polymer will effective if the polymer electrolyte is in the amorphous structure, and will not effective if in crystalline solid structure (the conductivity decreases).
3.2. Morphological characteristics

Surface morphology of the solid polymer electrolyte (SPE) of PVDF-HFP-LiBOB-TiO₂ was analyzed using SEM. Figure 2 shows the SEM images of SPE for all samples. These images indicate good compatibility between polymers, salts, and other contents.

They have a morphological shape such as a regular honeycomb structure with pore diameters of ±50 μm. From the SEM micrographs it was observed that pores formed in the A1 sample are not as much as in the A2 sample. While the sample A3 with an increase concentration of TiO₂ will actually reduce the number of open pores (covering other pores). It is because an addition of excess TiO₂ can cause agglomeration that it covers some of the pores that have been opened. The use of TiO₂ as filler in the formation of electrolytic polymer composites serves to reduce the crystalline fraction of the electrolyte in polymer composites. The more pore morphological forms or pores on the polymer electrolyte are expected to increase ionic reversibility during the redox process.

3.3. Thermal analysis

3.3.1. DSC analysis

Figure 3 shows the DSC thermograms of synthesized solid polymer electrolyte (SPE) sample with different amount of LiBOB salt and TiO₂ filler compositions. The PVDF-HFP membrane exhibits peak between melting temperature (Tm) of 125°C and 165°C. According to Saiki and Kumar, Tm of PVDF-HFP have calculated as 144.8°C [19]. This figure also shows that the presence of LiBOB salt causes the melting temperature (Tm) of PVDF-HFP increase up to 172.1°C. This shows that there has been an interaction of salt into the polymer system. Even, the addition of TiO₂ causes Tm continue to increase. In this experiment, the addition of TiO₂ was carried out up to 5% (A3 sample), and Tm
reaches 212°C. The thermograms also shows endothermic peaks at lower temperature that probably due to melting of different phases of PVDF crystals. Assuming that 100% crystalline melting point PVDF is 104.7 J g⁻¹, relative percentage of crystallinity (Xc) from polymer electrolytes can be calculated [19]. Table 2 shows melting point, enthalpy and relative percentage of crystallinity values for The SPE of PVDF-HFP/LiBOB and TiO₂ systems. The relative percentage of crystalline PVDF-HFP, Xc can be calculated using the equation as below:

\[ Xc = \frac{\Delta Hm_{complex}}{\Delta Hm} \times 100\% \]  

(1)

where \( \Delta Hm \) is the heat of fusion of PVDF-HFP. Table 2 shows that the A2 sample (70 wt% polymer, 28 wt% LiBOB salt and 2 wt% TiO₂) has the smallest relative percentage of crystallinity value.

3.3.2. TG analysis

Figure 4 shows the thermogram of synthesized solid polymer electrolyte (SPE) of PVDF-HFP- LiBOB with different concentration of LiBOB salt and TiO₂ filler compositions. Degradation occurs in a multi-step. This weight loss is due to SPE preparation using the solvent-casting technique in which some of the organic solvents are lost during evaporation. For A1 sample, the initial weight loss is started at 50-82.1°C and it is attributed to the loss of solvent and H2O from the surface and the mass loss of 4.4%, then continued from temperature of 82.3-119.8°C the mass loss of 3.7%.

Mass losses were about 9.06% at a temperature of 121.2 - 200°C. In contrast to the other two samples of A2 and A3, they appear to be more stable, since the mass loss is 1.8% for A2 sample and 3.06% for sample A3, respectively. These appearances can be said that an addition of TiO₂ will inhibit the removal of the sample weight because of the highly hygroscopic nature of the LiBOB salt and improvement of their mechanical properties. Thermal stability of the filler synthesized SPE can work at ± 100°C, which is suitable for designing lithium ion cells that are capable to operate at temperature higher than room temperature.

![Figure 3](image.png)  
**Figure 3.** DSC curves for the SPE of PVDF-HFP-LiBOB containing (A1) 0, (A2) 2, and (A3) 5 wt% of TiO₂.

![Figure 4](image.png)  
**Figure 4.** TGA curves for the SPE of PVDF-HFP-LiBOB containing (A1) 0, (A2) 2, and (A3) 5 wt% of TiO₂.

| Table 2. Melting point, melting enthalpy and relative percentage of crystallinity values for PVDF-HFP/LiBOB and TiO₂ systems. |
|-----------------|-----------------|-----------------|-----------------|
| Sample | \( Tm \) (°C) | \( \Delta Hm \) (J g⁻¹) | Xc (%) |
| A1 | 172.1 | -16.13 | 15.9 |
| A2 | 179.0 | -9.27 | 8.9 |
| A3 | 212.4 | -10.99 | 10.4 |
3.4. Ionic conductivity analysis

From figure 5, it can be observed that semicircle of impedance plots of PVDF-HFP-LiBOB containing 2 wt% TiO₂ (A2) was the lowest of the two other samples i.e. ~1000 Ω and ~2000 Ω respectively, and it shows that the ion conductivity of the A2 sample is twice larger than the other two samples. Equation $r = t_0 / (R_s \times A)$ is used to calculate the ionic conductivity, where $t_0$ is the thickness of the SPE and $A$ is the surface area of the SPE. From the equation, it can be shown that the smallest semicircle line intersecting x-axis indicates the greatest conductivity value. The addition of TiO₂ in the electrolyte polymer is useful for increasing ionic conductivity [19] but in this study, the addition of TiO₂ up to 5 wt% actually decreased the conductivity, as shown in figure 5. As the above explanation of morphological analysis, that adding 2 wt% TiO₂ will increase the formation of pores so that there is an increase in ionic reversibility during the redox process.

![Figure 5](image_url)

**Figure 5.** Impedance plots of the SPE of PVDF-HFP-LiBOB containing (A1) 0, (A2) 2, and (A3) 5 wt% of TiO₂ in an Li/Li cell.

However, the addition of excess TiO₂ will cause agglomeration so that it covers some of the pores. The reduced number of open pores causes a decrease in ionic reversibility during the redox process. With the increase in TiO₂ concentration, the LiBOB concentration automatically decreases, so the number of Li ions as electricity conductors decreases. The decrease in conductivity in sample A3 cause the amount of Li ions reductions and the number of pores is partially closed.

4. Conclusions

Solid polimer electrolyte (SPE) consisting of PVDF-HFP, LiBOB and TiO₂ have been prepared using solution casting method. Result of X-ray diffraction, SEM and DSC reveal the amorphous nature of electrolyte complex system for the same concentration of PVDF – HFP with different concentration of LiBOB and TiO₂. It is observed that semi crystallin nature gradually decreases up to optimum level and then increases. The complex formation between polymer, salt and filler was confirmed by XRD, SEM and DSC studies. The ionic conductivity for A2 sample with composition of 70 wt% polymer, 28 wt% LiBOB salt and 2 wt% TiO₂ is the largest. Based on the results of DSC and EIS analysis, the A2 sample has the smallest relative percentage of crystallinity value, and based on the result of the EIS analysis, ionic conductivity is twice larger than the other two samples. In addition, the effect of addition of TiO₂ in the A1 and A2 samples caused both of them having thermal stability that can work at ±100°C, which is suitable for designing lithium ion cells that are capable of operating at temperatures higher than room temperature.
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