The influence of TiO₂ composition in LiBOB electrolyte polymer composite membrane characteristics for lithium ion batteries applications

T Lestariningsih, Q Sabrina and E M Wigayati

Research Center for Physics - Indonesian Institute of Sciences, Kawasan Puspiptek, Tangerang Selatan, Indonesia

E-mail: titi013@lipi.go.id

Abstract. Characterization of the composite membrane of LiBOB electrolyte polymers made from poly (vinylidene fluoride co-hexafluororopylene) (PVdF-HFP) as the polymer, LiBOB or LiB(C₂O₄)₂ as electrolyte salt and titanium dioxide (TiO₂) as ceramic filler of three different concentrations have been done. Sample of membrane was prepared using solution casting technique. Microstructural study by SEM shows non-uniform distribution of pore over the surface of the sample. X-ray structural analysis, impedance spectroscopy, and cyclic voltammetry (CV) studies were carried out. Membrane composite polymer of LiBOB electrolyte without additional ceramic filler with composition of 70% polymer, 30% LiBOB, and 0% TiO₂ has the greatest conductivity for forming amorphous phase and is compatible with material membrane composite. Meanwhile, sample with 70% polymer composition, 28% LiBOB and 2% TiO₂ shows oxidation reaction at the most perfect discharge despite very slow current speed.

1. Introduction

Nowadays, the development of electrolyte membrane/polymer electrolyte is very attractive and continues to grow. One practical application from the polymer electrolyte membrane is that it can effectively be used as an electrolysis medium in energy storage devices such as battery. The other potential applications for modification of polymer and lithium salt is for fuel cell, sensors, and super capacitors [1]. Various sources of lithium salt such as LiFePO₄ [2], LiCF₃SO₃ [1], LiBF₄ [3], LiBOB [4] become electrolyte sources that have been developed as a source of Li⁺ charges in polymer matrix.

Lithium bis(oxalato) borate with chemical formula LiB(C₂O₄)₂ is the active ingredient of electrolyte in lithium battery. LiBOB is the main candidates substituting LiPF₆ which is highly toxic and harmful to human health. LiBOB electrolyte is considered to be more environmentally friendly because it compounds do not contain halogen element which is potential to pollute the environment. LiBOB also has high thermal stability of 302 °C [5].

Performance of lithium ion battery is based on the ionic conductivity (Li⁺ ions). Generally, conductivity is influenced by ion concentration as bearer charge and ion mobility [6] in accordance with equation:

\[\sigma = \sum n_i Z_i \mu_i\] (1)
where \( n_i \) is the amount of charge carrier, \( z_i \) the charge of ions, and \( \mu_i \) the mobility of ions. At the same condition of ion mobility, larger amount of lithium ions in the membrane results in increasing conductivity. However, if the \( \text{Li}^+ \) ion mobility condition is different, for example, ion mobility is smaller; it is possible that conductivity value will not always increase. Ionic conductivity is related to the polymer parts. The mobility of carrier is determined by the carrier environment itself, the interaction between the ions and the polymer, the flexibility of polymer chains and characteristics of carrier, and so on.

Electrolyte membrane is one type of electrolyte polymer. Electrolyte polymer is defined as a solution of alkali metal salt present in the polymer matrix [7]. The electrolyte membrane is formed by a polymer matrix having alkali metal ions as a source of its charges. Ions with low atomic mass such as lithium ions (\( \text{Li}^+ \)) will be easier to experience charge transport process. This transport is due to segmental relaxation in which the charge moves from one segment to another in the polymer matrix. The charge transport is more effective when polymer matrix is in the amorphous phase [8]. The simplest approach to grow amorphous phase is dispersed nanoparticle/ceramic filler in polymer matrix. The existence of nano-particles/ceramic filler dispersed among the polymer chains impedes their reconstruction in crystalline form [9].

Meanwhile, various polymers have been used as polymer membranes such as poly(vinylidene fluoride) (PVdF), poly(vinyl alcohol) (PVA), acetate cellulose, and polyacrylonitrile-methacrylate (P(AN-MMA)). Optimization of physical properties such as electrical conductivity becomes an important focus that still develops today. Poly (vinylidene fluoride-co-hexafluoropropylene) or PVdF-HFP is combined compound of polyvinylidene and hexafluoropropylene, and both of them are often functioned as a polymer forming electrolyte composite.

In this paper, fabricating polymer composite membrane of LiBOB electrolyte using PVdF-HFP and \( \text{TiO}_2 \) as filler with various compositions has been conducted as preliminary study. The aim is to find the influence of \( \text{TiO}_2 \) composition on the characteristics of polymer composite membrane of LiBOB electrolyte for lithium battery cell application. The manufacture of polymer composite membrane of LiBOB electrolyte was prepared by solution casting technique. The characterization involves investigating crystal structure, morphological structure, electrical conductivity and cyclic voltammetry (CV) testing for battery performance.

2. Experimental method

2.1. Material

Material used to fabricate electrolyte membrane were poly(vinylidene fluoride)-hydro furan phosphate (PVdF-HFP) as polymer (Sigma Aldrich), lithium bis(oxalato) borate (LiBOB) as lithium salts (Sigma Aldrich), titanium oxide (\( \text{TiO}_2 \)) as ceramic filler (Merck), and N,N-Dimethylacetamide (DMAc) solvents. Lithium ferro phosphate (LiFePO\(_4\)) from MTI and metal lithium were exploited as cathode and anode sheets. They were functioned for testing ion conductivity and cyclic voltammetry.

2.2. Sample preparation

Samples of LiBOB electrolyte membrane were made by solution cast technique. The first step was to make slurry (viscous solution) by dissolving LiBOB electrolytes salt and ceramic filler into DMAc solvent through mixing process using magnetic stirrer on a hot plate at temperature of 70-80 °C and speed of 240 rpm. The next step was adding PVdF-HFP as polymer matrix into the mixed solution with the same process to get slurry solution. Then, the solution was cast on a glass substrate and dried at room temperature.
2.3. Sample characterization

The first characterization of LiBOB electrolyte membrane was measuring ionic conductivity by EIS (Electrochemical Impedance Spectroscopy) method using LCR meter instrument, and HIOKI 3532150 Chemical Impedance Meters. This measurement was carried out in the form of coin cell that was applied in the form of half-cell battery. The half-cell battery used LiFePO₄ as the cathode and Li metal as the anode. Characterization of LiBOB electrolyte membrane included crystal structure characterized by XRD and morphology observation by SEM. Regarding the application of lithium ion batteries, samples were tested by cyclic voltammetry (CV), using WBCS3000 tool, Automatic Battery Cycler. CV testing was performed in the form of half-cells using LiFePO₄ as cathode and Li metal as an anode, while LiBOB electrolyte membrane serves as separator and electrolyte. Variations of samples in this study were figured out by table 1.

| Sample | PVdF HFP (% Weight) | Filler: TiO₂ (% Weight) | Commercial LiBOB salt (% weight) | Solvent |
|--------|---------------------|-------------------------|---------------------------------|---------|
| CPE-1  | 70                  | 0                       | 0                               | DMAc    |
| CPE-2  | 70                  | 30                      | 0                               | DMAc    |
| CPE-3  | 70                  | 0                       | 30                              | DMAc    |
| CPE-4  | 70                  | 2                       | 28                              | DMAc    |
| CPE-5  | 70                  | 5                       | 25                              | DMAc    |

3. Results and discussion

EIS (electrochemical impedance spectroscopy) is one of the methods to investigate electrical characteristics of materials. In the present study, impedance measurement by LCR meter instrument presented by Cole-Cole graph is shown by figure 1. Ionic conductivity of the electrolyte polymer composite can be calculated by using equation

\[ \tau = t / (Rb \cdot A) \]  

(2)

\( \tau \) is ionic conductivity, \( t \) is the sample thickness (cm), \( Rb \) is measured resistance, and \( A \) is cross-sectional area of the sample (cm²). \( Rb \) is obtained by determining semicircle line intersecting x axis. Measurement of ionic conductivity was only performed on CPE-3, CPE-4, and CPE-5 samples.

Conductivity measurement was carried out in the form of half-cells shown by Nyquist graph as figure 1. It shows that CPE-3 sample containing 70% polymer, 0% TiO₂, and 30% LiBOB salt has the smallest semi-circle shape. According to equation \( \tau = t / (Rb \cdot A) \), smaller semicircle line intersecting x-axis means greater conductivity value. Therefore, CPE-3 sample has the largest conductivity value. It can be seen from figure 1 that the addition of 2% TiO₂ will decrease conductivity value while adding 5% TiO₂ increases conductivity value. TiO₂ in polymer electrolyte promotes ionic conductivity. Adding TiO₂ is supposed to increase ionic conductivity. This phenomenon can be explained by the results of crystal structures and morphology analysis. XRD analysis was done to observe the change of crystalline properties due to the presence of Li⁺ metal ionic in polymer matrix. The maximum intensity is at an angle (2θ) of 28.078º. This peak is characteristic of polymer membrane (PVdF-HFP) and LiBOB.
Figure 1. Nyquist graph of sample of LiBOB electrolyte polymer composite in the form of coin cell with variation of TiO\(_2\) addition: CPE-3 (B), CPE-4 (D), and CPE-5 (F).

Figure 2 illustrates that adding 2% TiO\(_2\) changes amorphous structure into crystalline structure. Meanwhile, an addition of 5% TiO\(_2\) transforms crystal structures to amorphous structure. Therefore, membrane polymer has formed amorphous phase without adding TiO\(_2\) as demonstrated by figure 2. The existence of amorphous phase in electrolyte polymer membrane will support the effective segmental relaxation of the polymer. In crystalline solid phase, arrangement of chains will regularly reduce segmental relaxation, so that ionic transport (conductivity) becomes very low [10]. Consequently, the presence of amorphous phase turns out to be an important factor for increasing ionic conductivity in electrolyte membrane. That is why CPE-3 sample has the highest conductivity in half-cells. In addition, this phenomenon can also be proven by SEM analysis. SEM photographs of polymer electrolyte indicate good compatibility among polymer, salt, and other contents as well as the amorphous phase formation in the manufacture of electrolyte polymer composite. SEM images of CPE-3, CPE-4, and CPE-5 samples are shown in figure 3.

Figure 2. X-Ray diffractions patterns of composite polymer electrolyte.
Figure 3 demonstrates that CPE-3 sample with composition of 70% polymer, 0% TiO₂, and 30% LiBOB has good compatibility between polymers and salt, involving pore formation. CPE-4 sample with 2% TiO₂ addition does not show good compatibility among salt, polymer, and TiO₂, so amorphous phase transforms to crystalline phase. It is also evidenced by comparing the morphology of CPE-4 and the rutile TiO₂ sample [10] (figure 4).

![Images of CPE-3, CPE-4, and CPE-5](image)

**Figure 3.** Morphology of electrolyte polymer composite membrane of CPE-3, CPE-4 and CPE-5 samples with 20 kV at 5000x.

TiO₂ does not blend with polymers and salt (figure 4). However, adding 5% TiO₂ converts crystalline phase to amorphous phase as shown on figure 3c. Based on XRD and SEM analysis, CPE-3 sample without additional addition of TiO₂ has the highest conductivity when applied in half-cell. Nevertheless, with addition of 5% TiO₂ can transform crystalline phase to amorphous phase and increasing amount of TiO₂ may grow greater amount of amorphous phase.

![SEM microphotograph of composite polymer electrolyte for sample CPE-4](image)

**Figure 4.** SEM microphotograph of composite polymer electrolyte for sample CPE-4.

Considering the results of CV analysis in the form of cells containing LiFePO₄ as cathode and Li metal as an anode, CPE-4 sample has a very slow speed current to reach oxidation reaction at discharge condition (figure 5). By the type of cell testing, it was found that 2% TiO₂ added to the functional electrolyte decomposed just before the decomposition of the basic electrolyte at about just over 4.5 V. It was also confirmed that the highest impedance among the two other samples due to the film produced on catode was negligibly small, as displayed by figure 1.

4. Conclusions

LiBOB electrolyte polymer composite membrane of CPE-3 sample without adding TiO₂ has an amorphous phase, therefore it has highest conductivity properties among the three samples. CPE-4 sample with addition of 2% TiO₂ forms crystalline phase and materials composing membrane cannot mix or not compatible resulting in declining conductivity, but with adding 5% TiO₂ crystalline phase
starts to transform in amorphous phase resulting in increasing conductivity. However, with very slow current velocities, CPE-4 sample shows oxidation reaction at the most perfect discharge.

![Cyclic voltammograms of composite polymer electrolyte for sample (a) CPE-3, (b) CPE-4, and (c) CPE-5](image)

**Figure 5.** Cyclic voltammograms of composite polymer electrolyte for sample (a) CPE-3, (b) CPE-4, and (c) CPE-5

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