Study the synthesis of LiBOB compounds using lithium sources from sea water

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Abstract. Indonesia as a country rich in natural resources has a source of lithium that can be used as raw material for making LiBOB salt. Natural sources of lithium are found in seawater or brines, mineral rocks and in geothermal fluids. Seawater contains large amounts of NaCl so that it is possible to have Na impurities in Lithium obtained from seawater. In this research, LiBOB synthesis has been done using a source of lithium-containing Na. LiBOB is made by solid-state reaction method, where the raw material is mixed in solid condition, then heating in the furnace for calcination and sintering process. Sample analysis was carried out by comparing the synthesis of LiBOB using lithium sources containing Na with LiBOB synthesis using lithium sources without containing Na. Based on the results of the XRD analysis, it is showed that the content of 3% Na in the Lithium source does not affect changes in the LiBOB crystal structure. FTIR analysis showed that the content of 3% Na does not affect the formed LiBOB functional group, even though there is a shift in wave numbers. The results of the thermal analysis showed that both samples occurred endothermic reactions and had a decomposition temperature of around 300°C.

1. Introduction
The necessary energy become a something that is continuous and increases every year. Accordingly, research and development of energy are continuously carrying out until now. The battery is one of the most energy sources which has developed with the high capacity storage and heavyweight. The component of battery cell consists of electrolyte, electrode, separator, and the current collector. In principle, the battery uses an electrolyte with lithium salts such as LiPF₆, LiClO₄, LiAsF₆, LiBF₄, and LiBOB which was dissolved in carbonate alkyl organic solvent. Among these electrolyte salts, LiPF₆ has the highest conductivity properties. However, thermal of stability LiPF₆ is lower than other electrolyte salts.[1] LiBOB or lithium bis (oxalato) borate was developed as an alternative to replacing LiPF₆ which is more environmentally friendly due to LiBOB does not contain halogen element that is potentially contaminated environment [2-4].

Various LiBOB or lithium bis (oxalato) borate is the new salt that has investigated by Lischka et al. in Germany, these have excellent stability of electrochemical (~ 4.5 V) and highest relatively decomposition temperature in 320°C approximately. On the other hand, the stability of thermal and capacity retention of LiBOB is higher than LiPF₆ [1]. According to Bi-Tao Yu, et al. [5] reported that stability thermal of LiBOB at range 240 – 300°C and decomposition reaction of this material does occur at range temperature above 300°C.
The development of research about LiBOB salt was synthesized with different method or utilization of raw materials. Many researchers have been conducted about synthesis LiBOB such as ones that have been done by Bi-Tao Yu et al. [6] and Lestariningsih T et al[7], who synthesized LiBOB from the analytical grade material by the method of solid state reaction (powder metallurgy). The development of LiBOB was synthesized using Li$_2$CO$_3$ as a lithium source by Lestariningsih T et al [8].

Indonesia as a rich country with natural resources has lithium sources which can be utilized as raw material on the synthesis of LiBOB. In nature, the lithium sources can be found on seawater or brine, rock mineral and geothermal fluid. In the sea waters, there are 230 million tons lithium with low concentration ($\pm$ 0,178 ppm) [10]. The sea waters containing NaCl with many contents of that, it may contain the impurity of Na can be found. Therefore, in this paper, the influence of lithium sources which has to contain impurities of Na can be used as materials for making LiBOB without significantly reducing the quality of LiBOB was investigated. In this paper, there are many characterizations have been analyzed such as XRD, FTIR and STA. Solid state reaction method was employed in this research for the synthesis of LiBOB using an established method. Sample preparation LiBOB compound was prepared the reaction path as follows [6-9]:

$$2\text{H}_2\text{C}_2\text{O}_4\cdot\text{2H}_2\text{O} + \text{LiOH.H}_2\text{O} + \text{H}_2\text{BO}_3 \rightarrow \text{LiB(C}_2\text{O}_4)\text{2} + 9\text{H}_2\text{O}$$  \hspace{1cm} (1)

In this reaction, oxalic acid dihydrate, lithium hydroxide and boric acid were mixed with molar ratio 2:1:1, furthermore the samples were sintered at the suitable temperature to obtain the LiBOB. This method was simple, easy to do and high safety for environments that organic solvent reaction method [9].

2. Experiment

In the synthesis of LiBOB, oxalic acid dehydrates ($\text{H}_2\text{C}_2\text{O}_4\cdot\text{2H}_2\text{O}$), boric acid ($\text{H}_2\text{BO}_3$), lithium hydroxide (LiOH) and sodium chloride (NaCl) were used as reactants. These materials were obtained in analytical grade (Merck). The materials were homogeneously mixed with grinding mill at 2:1:1 molar ratio for oxalic acid dihydrate, boric acid and material mixed (LiOH + NaCl). The variation of samples in this experiment is the percentage of NaCl against lithium source from LiOH, as shown in table 1. Heat treatment was performed using Thermolyne muffle furnace in two steps; the first step at temperature 120 °C for 4 hours, and the second step at 240 °C for 6 hours. In this study, LiBOB salt was synthesized using a lithium source with containing impurities of Na with the percentage of NaCl to LiOH variations. They were compared with LiBOB salt synthesized without the addition of NaCl as a lithium source. This method of synthesis LiBOB refers to experiments by Bi Tao Yu et al [6] and Lestariningsih T et al [9].

Powder crystallinity was investigated using X-Ray Diffractometer (XRD) Rigaku type SmartLab, with CuK$\alpha$ target, wavelength $\lambda = 1.5406$ Å, and 2θ range of 10° to 45°. A diffractogram with diffraction peaks was found as a result and information has been formed phase as qualitative analysis in form of crystal structure parameter was obtained with Rietveld method using Highscore software analysis. In addition, to confirm the phase of LiBOB was analyzed using FT-IR spectroscopy Thermo scientific type Nicolet iS-10 to know the functional group. FT-IR spectroscopy scanning was made within wavenumber range of 4000 to 500 cm$^{-1}$ with the ATR method. FTIR is only carried out on the sample that most optimally forms the LiBOB phase. In addition to FTIR analysis, confirmation of the optimal formation of the LiBOB phase is also analyzed using thermal properties. Thermal properties were detected by using differential scanning calorimetry (DSC–Linseis) and thermal gravimetric analysis (TGA – Linseis). The temperature range was 0 °C to 400 °C at the heating rate of 10°C/min.

Details on the composition of the studied samples, i.e., with variations of the percentage of NaCl to lithium source LiOH, are summarized in Table 1.
Table 1. The composition of the LiBOB samples studied in this work

| No | Sample name     | H₂C₂O₄·2H₂O | H₃BO₃ | LiOH = 1mol LiOH (wt%) | NaCl (wt%) |
|----|----------------|-------------|-------|------------------------|------------|
| 1  | LiBOB – PA     | 2 mol       | 1 mol | 100                    | 0          |
| 2  | LiBOB - Na 3%  | 2 mol       | 1 mol | 97                     | 3          |
| 3  | LiBOB - Na 10% | 2 mol       | 1 mol | 90                     | 10         |
| 4  | LiBOB - Na 20% | 2 mol       | 1 mol | 80                     | 20         |

3. Result and Discussions

LiBOB synthesis has been successfully carried out with lithium sources containing various concentrations of Na, in this paper referred to as LiBOB-Na samples and LiBOB synthesis with lithium without Na sources, referred to as LiBOB -PA. The XRD curves between LiBOB-Na samples with various concentrations compared with the LiBOB-PA sample, as shown in Figure 1. Analysis using X-Ray Diffractometer aims to determine the phase formation of LiBOB material.

Figure 1. Figure X-ray diffraction analysis of LiBOB-PA, LiBOB Na-3%, LiBOB Na-10%, and LiBOB Na-20%.

Figure 1 exhibits the XRD curves of LiBOB with lithium sources containing various concentration Na and LiBOB – PA. All of the curves, LiBOB with lithium sources containing various concentration Na which is expected to have formed, but there are still many impurities including water content and boric acid which is not reacting. The results show that the phases formation of LiBOB is LiBOB hydrate with the value of angles (2θ) 19.378°, 20.100°, and 23.762° (ICSD 98-005-9985) and LiBOB phase has the highest intensity at angles (2θ) 9.380°, 23.931° and 27.069° (ICSD 98-028-1623). In the value of angles (2θ) 14° and 28°, the intensity of boric acid (H₃BO₃) enhance as increasing the concentration Na with reference data (ICSD 98-002-4711).

Based on the results of data processing using the Rietveld method, the percentage of phase and parameter unit cells of samples were presented in Table 2. According to Tables 2, the table showed that synthesis LiBOB using lithium source containing concentration Na to 20% can form LiBOB with orthorhombic structure. The parameter unit cells, volume and density of LiBOB – Na 3% have a similarity with LiBOB – PA. The formation of LiBOB hydrate phase for the sample containing different concentration Na has a relatively similar with the sample of LiBOB – PA. The composition phase of LiBOB hydrate with the sample of LiBOB Na 3% has an approximately similar value with the sample of LiBOB – PA. The enhancement of concentration Na in the lithium sources cause slightly amount formation of LiBOB hydrate, but the phase of LiBOB has increased. It may cause by containing of Na ion which that binding the water molecular. It means that the impurity of Na will reduce the hygroscopic properties of LiBOB compounds, although the presence of Na will increase the
amount of boric acid. This also indicates that the reaction of LiBOB synthesis has not occurred perfectly. Boric acid is one of the main ingredients for LiBOB synthesis. Figure 1 shows that at an angle of 14° and 28°, there is an increase of intensity was exhibited by an increasingly high peak. (Increasingly high peaks shows increase of intensity at the angle of 14° and 28° (Figure 1)). The peak is the peak of the boric acid phase (H₃BO₃). Based on Tables 2, it can be concluded that the maximum to synthesize the LiBOB compounds with impurity Na in the lithium source is 3%.

Table 2. Crystallographic data of synthesized LiBOB sample from Rietveld refinement

| Sample         | Indicated phases | Lattice parameter and unit cell volume | Lattice system | The composition of the phase (%) | Density (g/cm³) |
|----------------|------------------|---------------------------------------|----------------|----------------------------------|-----------------|
| LiBOB – PA     | LiBOB            | 6.373 7.569 13.172 635.4             | Orthorhombic   | 0.7                              | 2.03            |
|                | LiBOB hydrate    | 5.619 16.124 15.926 1442.9           | Orthorhombic   | 98.4                             | 1.95            |
|                | H₃BO₃            |                                       |                | 0.9                              |                 |
| LiBOB – Na 3%  | LiBOB            | 6.368 7.572 13.164 634.7             | Orthorhombic   | 0.7                              | 2.03            |
|                | LiBOB hydrate    | 5.612 16.109 15.902 1438.1           | Orthorhombic   | 96.5                             | 1.96            |
|                | H₃BO₃            |                                       |                | 2.8                              |                 |
| LiBOB – Na 10% | LiBOB            | 6.044 7.524 13.388 606.7             | Orthorhombic   | 4.8                              | 2.12            |
|                | LiBOB hydrate    | 5.610 16.105 15.899 1436.5           | Orthorhombic   | 63.5                             | 1.96            |
|                | H₃BO₃            |                                       |                | 31.7                             |                 |
| LiBOB – Na 20% | LiBOB            | 5.612 16.115 15.893 606.7             | Orthorhombic   | 5.8                              | 2.12            |
|                | LiBOB hydrate    | 5.612 16.115 15.893 1437.4           | Orthorhombic   | 47.4                             | 1.96            |
|                | H₃BO₃            |                                       |                | 46.8                             |                 |

Furthermore, the LiBOB Na 3% sample was confirmed by FTIR analysis to determine the formation of functional groups by comparing the results of the sample FTIR analysis of LiBOB-PA. Figure 2 shows the infrared spectrum for samples of LiBOB-PA and LiBOB-Na 3%. Based on Figure 2, it can be seen that LiBOB Na 3% has a functional group similar to the LiBOB PA sample although there is still a significant shift in wavelength. The figure represents that 3% Na impurity can cause a longer percentage of transmittance or a stronger absorption. Strong, weak absorption or the amount of energy absorbed depends on the type of bond that exists in the compound. The type of polar bond exhibit a strong absorption, while the non-polar bond causes weak absorption [11]. These differences in absorption strength are partly due to changes in dipole moments when energy is absorbed.

Figure 2. Comparison of the Infrared spectra of the sample of LiBOB-PA and LiBOB-Na 3%
Table 3. Functional groups and absorption bands of reference, LiBOB –PA and LiBOB-Na 3%

| Functional groups          | Wave number of reference (cm\(^{-1}\)) (Aravin and Vickraman, (007)[12] | Wave number of LiBOB-PA (cm\(^{-1}\)) | Wave number of LiBOB-Na3% (cm\(^{-1}\)) |
|---------------------------|---------------------------------------------------------------------------|----------------------------------------|------------------------------------------|
| O-H                       | -                                                                         | 3513                                   | 3514                                     |
| C=O oscillate in phase and out of phase | 1811,1779                                                              | 1809,1796                              | 1813,1797                                |
| C=O stretch               | 1750                                                                     | 1769                                   | 1768                                     |
| COO\(^{-}\) asymmetric stretch | 1640                                                                     | 1633                                   | 1652                                     |
| C-H stretch               | 1442                                                                     | 1447                                   |                                          |
| B-O stretch               | 1372                                                                     | 1304                                   | 1307                                     |
| C-O-B-O-C stretch        | 1297                                                                     | 1274                                   | 1273                                     |
| C-O-C asymmetric stretch | 1215                                                                     | 1230                                   | 1229                                     |
| O-B-O symmetric stretch | 1070                                                                     | 1083                                   | 1082                                     |
| O-B-O symmetric and asymmetric stretch | 999, 982                                                            | 996                                    | 995                                      |
| COO\(^{-}\) deform       | 708                                                                      | 713                                    | 712                                      |
| B-O deform               | 604                                                                      | 614                                    | 615                                      |

In the LiBOB Na 3% infrared spectrum, it can be seen that there are functional groups C-O, C = O, B-O, and O-B-O as shown in Figure 2.a. Wave numbers 1768-1813 cm\(^{-1}\) indicate the appearance of groups C = O and wave numbers 995-1273 cm\(^{-1}\) indicating the presence of C-O-B-O-C. According to Aravin and Vickraman (2007) [12], absorption bands must appear at wave numbers 982 cm\(^{-1}\) and 1008 cm\(^{-1}\) for LiBOB compounds, but the absorption band on the wave number does not appear on LiBOB-Na 3%. The wave number 3514 cm\(^{-1}\) indicates the presence of an O-H group, which indicates the possibility of an imperfect reaction between H\(_3\)BO\(_3\) or H\(_2\)C\(_2\)O\(_4\) to form LiBOB. It can also mean the presence of hydroxyl groups in water vapor caused by hygroscopic LiBOB properties. Based on the description above, it can be said that the NaCl impurity does not cause functional group changes but causes a slight shift in wave numbers and a longer / stronger transmittance percentage. In addition to FTIR analysis, the LiBOB Na-3% sample was also confirmed by thermal analysis to determine the reaction type and decomposition temperature of LiBOB compounds with lithium sources containing Na.

Figure 3. Comparison of differential scanning calorimetry (DSC) sample of LiBOB - PA and LiBOB-Na 3%
Thermal analysis with DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis) was carried out to determine the physical properties of the sample is treated with heat. Figure 3. present that all reactions that occur in both samples are endothermic. In LiBOB- Na 3% sample, a water molecule release reaction occurs from the reaction of oxalic acid hydrate (H$_2$C$_2$O$_4$ • 2H$_2$O) with Lithium hydroxide (LiOH) at a temperature of about 93.5 °C while in the LiBOB-PA sample at a temperature of about 99.7 °C. The second endothermic peak that occurs at temperatures above 150 °C begins to happen in the formation of LiBOB compounds. LiBOB compounds in both samples were formed and stable at a temperature range of about 225-250°C. Decomposition reactions of LiBOB compounds in the two samples began to occur at temperatures around 305°C to form Li$_2$C$_2$O$_4$, B$_2$O$_3$, CO$_2$ and CO compounds. TGA analysis for LiBOB-PA and LiBOB –Na 3% samples are shown as in Figure 4.

From Figure 4, it can be seen that the decrease in mass begins to occur at a temperature of around 90°C, caused by the release of water molecules. The reduction in duration is 41.434% for LiBOB-Na samples of 3% and 34.962% for LiBOB-PA. The amount of mass reduction in the LiBOB-Na sample is 3% greater because in addition to the release of water molecules that begin earlier also the possibility of other compounds due to impurities Na. The decomposition process of LiBOB occurs at a temperature of about 300°C trapping, and there is a period of 31.81% decrease for LiBOB-Na 3% and 30.53% for LiBOB-PA samples. According to the comparison between the results of the analysis of TGA LiBOB-PA and LiBOB-Na 3%, the percentage decrease mass in LiBOB -Na 3% is greater than the percentage decrease in the mass of LiBOB -PA.

4. Conclusions

LiBOB synthesis has been successfully carried out with lithium sources containing of Na, in this paper referred to as LiBOB-Na samples and LiBOB synthesis with lithium without Na sources, referred to as LiBOB-PA. Based on XRD, FTIR and thermal analysis, it can be concluded that the maximum to synthesize the LiBOB compounds with impurity Na in the lithium source is 3%. The results of the XRD analysis showed that the enhancement of concentration Na in the lithium sources cause slightly amount formation of LiBOB hydrate, but the phase of LiBOB has increased. The results of FTIR analysis shows that LiBOB Na 3% has a functional group similar to the LiBOB PA sample although there is still a significant shift in wavelength. The results of differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) showed that the 3% LiBOB-Na sample formed the endothermic reaction, the formation temperature and decomposition temperature of the LiBOB compound was almost the same as the LiBOB-PA sample.
The results of this study can be used as a reference for further research on the synthesis of LiBOB electrolyte salts using lithium sources from abundant seawater.

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