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Synthesis and Characterization of LiBOB Material as an Electrolyte

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ABSTRACT: Inside battery, the electrolyte becomes a very important electrochemical device. The electrolyte functions as a transfer medium for Li ions in the battery. One of the salts that can cover the deficiency of LiPF6 as an electrolyte material currently widely used is LiBOB (Lithium BisBorate) salt material. Lithium bis (oxalato) borate material, a new lithium salt, was first introduced in 1999 by Xu et al, which is currently being developed as a replacement electrolyte for lithium-ion batteries. LiBOB is a promising electrolyte material regarding battery safety since judging from the potential for excess salt supported by previous research, LiBOB can be the answer to the problem of using electrolytes that are not environmentally friendly. The synthesis of LiBOB refers to Wigayati (2018) which was modified by replacing the LiOH material with Li2CO3. The ingredients lithium carbonate, boric acid and oxalic acid were prepared first with weigh and mix based on molar ratio 1 : 2 : 5. The synthesis was carried out by the solid-state reaction method. Crystals were characterized by FTIR, SEM-EDX, XRD and AAS. From the results of the SEM test, it was found that the LiBOB particles had spherical and cylindrical shapes, and there were Na impurities due to the raw material H3BO3. In the XRD test, it was found that the LiBOB hydrate phase matched at 2-theta 23.7641°, 20.1454° and 19.438°. As well as the LiBOB phase matched at 2-theta 19.438°, 23.4669° and 27.1796°. The FTIR test results found the same wave as the Wigayati reference chart. In the AAS test, it was found that Na and Li metals were contained in the synthesis sample.

Keywords: Electrolyte, Battery, Lithium, Lithium bis(oxalate) borate, Characterization, Sintering

1. Introduction

Energy is an important aspect of daily activities, especially in the digital era, which is currently being intensively implemented in all aspects. Human mobility depends on digital goods that require energy stored in electric storage devices. Batteries are the

most efficient source of energy storage for use in the mobility of human life. At present, lithium-ion batteries are the most widely used batteries because of their high voltage, high energy density, good cycle ability, and good stability at high temperatures. Inside the battery, the electrolyte solution becomes a very important electrochemical device. The electrolyte functions as a transfer medium for Li ions in the battery from the cathode to the anode during charge and from the anode to the cathode during discharge, so that lithium salts are an important component in the electrolyte. To obtain optimal capacity, electrolyte materials must have high ionic conductivity, good electrochemical stability, have good chemical stability so that they are not reactive with electrodes and separators, and are environmentally friendly [1]. Currently LiPF6 (Lithium Hexafluorophosphate) electrolyte is widely used in lithium-ion batteries, including anode-free lithium-ion batteries, with a salt conductivity of >10 mS/cm. However, the retention capacity and thermal stability of LiPF6 are still low [5]. This makes LiPF6 unstable at high temperatures, and even decomposes into LiF and PF5 , where these compounds are very dangerous and detrimental to battery performance, that the compounds can react with water to form HF which has the potential to damage battery cathode cells [3]. On the other hand, one of the salts that can make up for the lack of LiPF 6 is the salt material LiBOB (Lithium Bis(oxalate) borate). Lithium bis (oxalato) borate material is a new lithium salt which was first introduced in 1999 by Xu et al [4], which is currently being developed as a replacement electrolyte for lithium-ion batteries. LiBOB is a promising electrolyte material regarding battery safety. LiBOB has good electrochemical stability (~4.5V) and a fairly high decomposition temperature (around 320°C). This property means that LiBOB has better thermal stability, when compared to LiPF6 which decomposes at 177 – 200 °C. In addition, the results of the last few years by several researchers have published LiBOB, including LiBOB thermal studies which show good performance of the material as a electrolyte at 300°C. The rest, LiBOB will be decomposed into Li_2CO_3, B_2O_3, and CO_2. In addition, the economic value of LiBOB is also relatively cheap compared to other materials, so it is widely used in lithium batteries [4] .

From the potential for excess salt supported by previous research, LiBOB can be the answer to the problem of using electrolytes that are not environmentally friendly. Research on LiBOB is important because LiBOB is a potential substitute for LiPF6 which is not environmentally friendly and harmful to human health.[8] The potential possessed by LiBOB can be explored further with the synthesis carried out. LiBOB is easy to manufacture, environmentally friendly, and less expensive. LiBOB is synthesized using the solid-state reaction method which is easier, simpler and environmentally friendly [1]. The raw material for the lithium source used is Lithium Carbonate (Li_2CO_3). Characterization was also carried out to determine the microstructural analysis of LiBOB to obtain data on the surface of the material, crystal characteristics and crystal density, as well as material functional groups.

2. Experimental Method

2.1 Material

The main materials in this research consists of demineralized water as a purification agent, Oxalic acid ($C_2H_2O_4$) as crystal forming agent (Merck ≥ 99,5%), Lithium carbonate (Li_2CO_3) as lithium sourcing agent (Merck ≥ 99%), Boric acid (H_3BO_3) as borate source agent (from own synthesis).

2.2 Methodology

This research runs out with two steps to synthesis the material. The first is LiBOB synthesis which is purposed to make synthesis salt with solid state method [6][7]. Then, the final step is characterized and interpretation test to make sure and know the characteristic of salt is appropriate to commercial LiBOB.

2.2.1 LiBOB Synthesis

The synthesis of LiBOB refers to Wigayati (2018) [6] which was modified by replacing the LiOH material with Li_2CO_3. The process flow can be seen in figure 1. The reaction mechanism that occurs in the synthesis of LiBOB salt from Li_2CO_3 is as follows

$$Li_2CO_{3(s)} + 2H_3BO_{3(s)} + 5H_2C_2O_{4(s)} \rightarrow 2LiB(C_2O_4)_{2(s)} + 3CO_{2(g)} + 7H_2O_{(g)}$$

The materials lithium carbonate, boric acid and oxalic acid were prepared first with weigh and mix based on molar ratio 1: 2: 5. Then it was heated in a muffle furnace at 120°Cfor 4 hours, and at 240°C for 15 hours. The results of heating are in the form of white LiBOB crystals which are then crushed with a mortar and sieved with a 200-mesh sieve. Crystals were characterized by FTIR, SEM-EDX, and XRD.

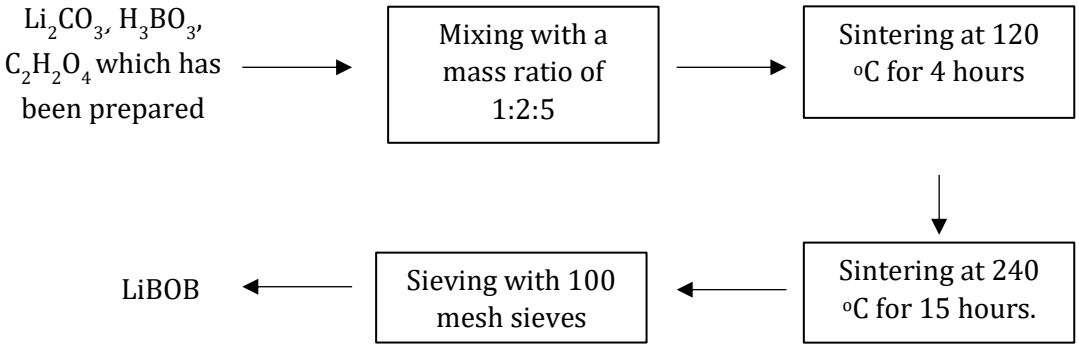

Figure 1. Process flow of LiBOB synthesis

2.2.2 Data Characterization and Interpretation Test

The synthesis salt was characterized with Scanning Electron Microscopy – Energy Dispersive X-Ray (SEM-EDX), X-Ray Diffraction (XRD), Fourier transform Infrared Spectroscopy (FTIR), and Atomic Absorption Spectroscopy (AAS). First SEM-EDX on the synthesized LiBOB salt is carried out to determine the atomic/substance content contained therein. The tool used is the JEOL Benchtop Scanning Electron Microscopy JCM 7000 which was carried out at the Pusat Unggulan IPTEK (PUI) Baterai UNS. Second is XRD test on the synthesized LiBOB salt was carried out to determine the structure of the crystal system in the material using the MD10 X-Ray Diffractometer (MTI, USA) in the range of 2θ from 18-67o using CuK-α anode ray λ = 1, 54178Å which was carried out at the Pusat Unggulan IPTEK (PUI) Baterai UNS.

Then third is FTIR test on the synthesized LiBOB salt was carried out to analyze the functional groups in the material using the Shimadzu IR Spirit equipment which was carried out at the Pusat Unggulan IPTEK (PUI) Baterai UNS. The last is AAS test on the synthesized LiBOB salt was carried out to analyze the metals contained in the material using the Shimadzu AA 7000 tool which was carried out at the Pusat Unggulan IPTEK (PUI) Baterai UNS.

3. Results and Discussion

In An Observation of the morphology of LiBOB particles from sintering was evaluated using scanning electron microscope (SEM). SEM Characterization provides information regarding the

morphology and size of the samples tested. Samples characteristic was tested at 500x, 1000x, 2500x, and 5000x magnification. The morphological results obtained are shown in Figure 1. In Figure 2. the samples show that the particles are still agglomeration and the form of LiBOB particles are spherical and cylindrical [2].

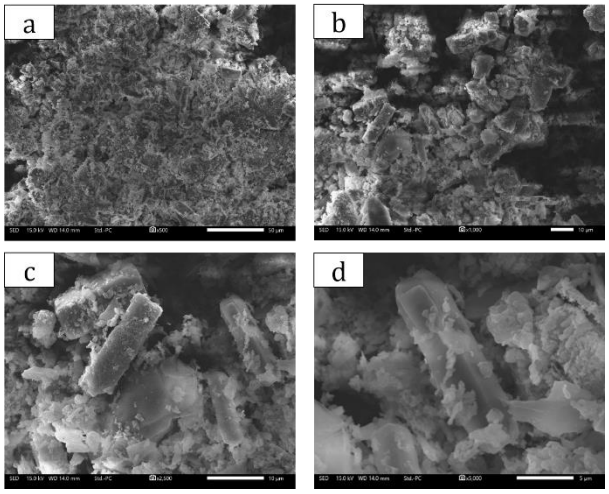

Figure 2. SEM morphology of LiBOB with magnification (a) 500x, (b) 1000x, (c) 2500x, and (d) 5000x

Table 1. shown the result of EDX characterization testing of LiBOB. In the table, it is known that the largest element weight in LiBOB is element O with mass percentage = 73.94 ± 1,36%, then Na = 12.39 ± 0.66%, B = 7.54 ± 0.32% and C = 6.13 ± 0.33. Element of Na should not be found in LiBOB compound. This is because the raw materials used contain Na elements, this is proven by EDX testing on each raw material and shown in Table 2. But the Li element cannot be analyzed using EDX, so further testing is needed to determine the presence or absence of Li elements in the LiBOB.

Table 1. Elemental mass percentage of LiBOB with EDX analysis

Element	%Mass	%Atom
B	7.54 ± 0.32	10.95 ± 0.46
C	6.13 ± 0.33	8.01 ± 0.43
O	73.94 ± 1.36	72.58 ± 1.33
Na	12.39 ± 0.66	8.46 ± 0.45
Total	100.00	100.00

Based on Table 2.c, the source of Na comes from boric acid as raw materials. This is because the boric acid used is a compound synthesized from Pusat Unggulan IPTEK (PUI) Baterai UNS. So that the level of impurities in these raw materials is still quite a lot.

Table 2.a. Elemental mass percentage of Li_2CO_3 as raw material with EDX analysis

Element	%Mass	%Atom
C	13.86 ± 0.41	17.64 ±0 .53
O	86.14 ± 1.41	82.36 ± 1.35

Total	100.00	100.00

Table 2.b. Elemental mass percentage of $H_2C_2O_4$ as raw material with EDX analysis

Element	%Mass	%Atom
C	18.32 ± 1.45	23.00 ± 1.83
O	81.68 ± 4.55	77.00 ± 4.29
Total	100.00	100.00

Table 2.c. Elemental mass percentage of H_3BO_3 as raw material with EDX analysis

Element	%Mass	%Atom
O	73.11 ± 1.11	79.62 ± 1.21
Na	26.89 ± 0.90	20.38 ± 0.68
Total	100.00	100.00

AAS testing is used to determine the metal content of LiBOB compounds. This test is needed to find out whether the resulting LiBOB contains Li elements or not. Table 4 shows the calibration curve of AAS testing on LiBOB samples. Based on the test results, it was known that in the sample there are two metal elements, there are Li metal and Na metal

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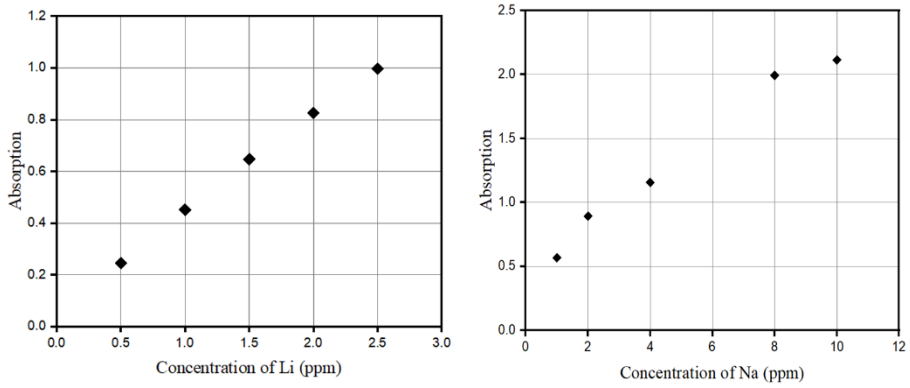

Figure 3. Calibration curve of Li and Na during AAS

From the two calibration curves in figure 3, the linear equation is obtained as follows:

$$Abs\ (Li) = 0.37584conc + 0.069960 \quad (1)$$

$$Abs\ (Na) = 0.16898conc + 0.55974 \quad (2)$$

The results of the AAS test are known to be the concentration of metal in LiBOB compounds under certain dissolution conditions. The concentration of Li metal is known at dissolving conditions of 1:10,000 and 1:100,000, while the concentration of Na metal has been seen at dissolving conditions of 1:100 and 1:1000.

Table 3. Elemental concentration of Li and Na presence in LiBOB

Li		Na	
VF : DF	ppm	VF : DF	ppm
1:10,000	0.5825	1:100	14.2603

1:100,000	0.0504	1:1,000	11.4197

Characterization of LiBOB using FTIR was aimed to identify the functional groups contained in the LiBOB compound. Figure 4. shows the infrared spectrum of synthesized LiBOB. The functional groups in the LiBOB synthesis result correspond to references to commercial LiBOB functional groups, can be seen in Table 3.

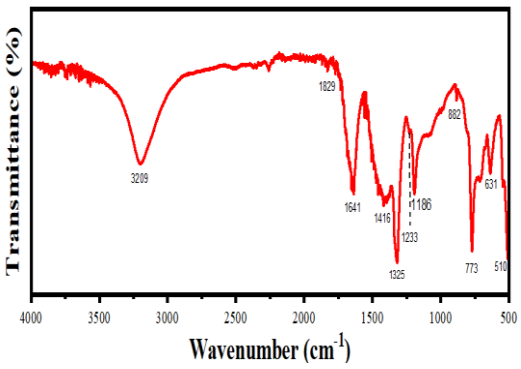

Figure 4. FTIR spectrum of LiBOB powder

Table 4. Functional groups and absorption bands of synthesized LiBOB and commercial LiBOB as reference

Functional Groups	*Wavenumber* (cm^{-1}) Commercial LiBOB [6]	*Wavenumber* (cm^{-1}) LiBOB Synthesis
OH	3441	3209
C=O *oscillate in phase and out of phase*	1818 ; 1781	1829
COO^- *asymmetric stretch*	1639	1641
COO^- *asymmetric stretch*	1443	1416
B-O *stretch*	-	1325
C-O-B-O-C *stretch*	1307	-
C-O-C *asymmetric stretch*	1222	1233
O-B-O *symmetric stretch*	1088	1186
O-B-O *symmetric and asymmetric stretch*	998/983	882
COO^- *deform*	709	773
B-O *deform*	607	631
BO_4 *bond*	492/480	510

According to Lestariningsih et al (2017), the absorbtion bands should appear on LiBOB powder in wave numbers 1740 – 1820 cm^{-1} (C = O absorbtion bands), wave number 980 – 1370 cm^{-1} (C = O stretch and B – O absrbtion bands), and the emergence of lithium oxalate in wave numbers around 1658 and 778 cm^{-1} [9].

X-ray diffraction pattern (XRD) of synthesized LiBOB was presented on Figure 3. XRD was carried put at a value of 2-theta = 10^o – 80^o with a wavelength of Cu-Kα (1.541874Å). Based on X-ray diffraction pattern of this sample, it was indicated that there were two phase of LiBOB, there are $LiB(C_2O_4).H_2O$ (LiBOB Hydrate) and $LiBC_4O_8$ (LiBOB). The LiBOB hydrate was indicated from ICDD database no. 01-073-9447 at 2-theta 23.7641^o, 20.1454^o, and 19.438^o and the LiBOB was indicated from ICDD database no. 00-062-0917 at 2-theta 19.438^o, 23.4669^o, and 27.1796^o. Based on Figure 5, there are several peaks that are not in accordance with the ICDD database. This is due to the presence of impurity

elements such as Na in the content of LiBOB compounds [9].

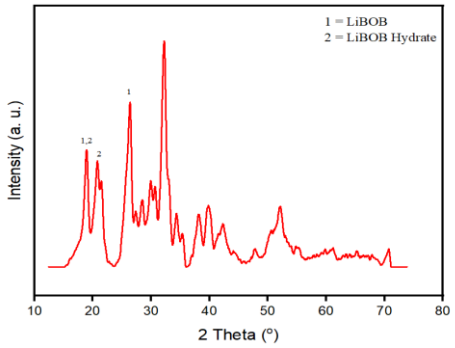

Figure 5. XRD pattern of LiBOB powder

4. Conclusion

LiBOB material was successfully obtained from Li_2CO_3, although the content of impurities of the Na element is quite large due to the raw materials used thus causing a slight discrepancy with the reference. As shown in the result of the characterization test, in SEM-EDX and AAS testing, the content of LiBOB material is in accordance with its constituent elements. FTIR test confirmed the presence of LiBOB functional groups. And the resulting XRD peaks match according to ICDD data on LiBOB and LiBOB hydrate.

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Author Contributions

Ardian Febrianto and Annisa Salsabila Ghina Muthi carried out the experiment and wrote the manuscript with a helpful support from Muhammad Nur Ikhsanuddin as Assistant Supervisor and Agus Purwanto as supervisor of the overall project. The final report was committed by all contributors.

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