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ORIGINAL PAPER

Synthesis and characterization of LiBOB as electrolyte for lithium-ion battery

Etty Marti Wigayati[1] · Titik Lestariningsih[1] · Achmad Subhan[1] · Christin Rina Ratri[1] · Ibrahim Purawiardi[1]

Abstract A synthesis process of lithium bis(oxalato) borate (LiBOB) has been conducted. LiBOB is one of lithium salts which is potentially viable to be utilized as an electrolyte material for lithium-ion battery. In the synthesis of LiBOB powder, oxalic acid, lithium hydroxide, and boric acid were mixed with 2:1:1 mol ratio until homogeneous. The method employed in the synthesis of LiBOB was solid state reaction. According to the result analysis from a differential thermal analyzer (DTA) equipment, it was decided that the first heat preservation should be carried out at 120 °C for 4 h, and then heating temperature for preparing LiBOB was at 240 °C for 7 h. The crystal structure of the LiBOB powder formed from the heating process was analyzed with X-ray diffractometer (XRD). The data found were further explored to determine the phase formed, to calculate percentage of synthesized LiBOB from the crystallography data. The dominant phases formed were LiBOB and LiBOB hydrate, and impurities in another phase were also presented. The result of Fourier transform infra red (FTIR) spectroscopy within wave number range of 500–4000 cm^{-1} confirmed that functional group of $LiB(C_2O_4)_2$ compound was found, identified by the appearance of absorption band C-O, C=O, B-O, O-B-O, and C-C. LiBOB microstructure which was observed with scanning electron microscope (SEM) is also presented. Furthermore, LiBOB powder was made into liquid electrolyte with carbonate-based solvent, and tested in a half-cell lithium-ion battery which is characterized on the cyclic voltammetry (CV) curves.

Introduction

The demand for lithium-ion batteries as advanced power sources has increased recently due to its high-capacity energy storage. The most commonly used electrolyte in Li-ion batteries is $LiPF_6$, which has high specific conductivity (>10 mS cm^{-1}) in alkyl carbonate mixtures [1]. $LiPF_6$ is usually dissolved in a mixture of ethylene carbonate (EC) and linear esters such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and/or ethyl methyl carbonate (EMC). The combinations of these components possess several undesirable characteristics; $LiPF_6$ is not stable at higher temperatures and decomposes into LiF and PF_5. PF_5 and $LiPF_6$ also react with water to form HF which can destroy the cell cathode [2, 3].

In its early researches by Xu et.al, lithium bis(oxalato) borate (LiBOB) was regarded as the most promising alternative as electrolyte for solid lithium-ion batteries [4]. LiBOB solutions in alkyl carbonates were found to be much more thermally stable than $LiPF_6$ solutions, have low cost, and have low susceptibility [5]. In addition, the capacity retention of LiBOB-based electrolyte is relatively higher than $LiPF_6$ when exposed in a half-cell battery up to 100 cycles [6]. Especially, it can effectively stabilize the graphite structure even in pure propylene carbonate (PC) and facilitate the formation of solid electrolyte interface (SEI) on the surface of carbonaceous anode materials [7].

✉ Etty Marti Wigayati
etty001@lipi.go.id

Christin Rina Ratri
christin.rina.ratri@lipi.go.id

[1] Research Centre for Physics, Indonesian Institute of Science, Kawasan Puspiptek, Serpong Tangerang 15314, Indonesia

⌷ Springer

Fig. 1 DTA thermogram of materials mixture: LiOH, $H_2C_2O_4.2H_2O$, and H_3BO_3
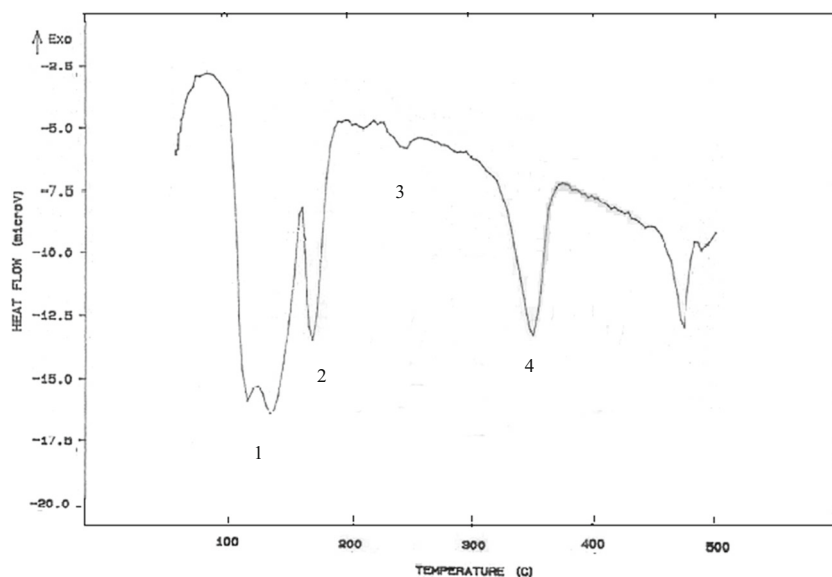
In this work, we report on the synthesis of LiBOB at optimum heat preservation and heating temperature conditions based on the kinetics study [8] and thermal behavior of LiBOB [9]. The method employed in the synthesis of LiBOB was solid state reaction; this method was easier, cheaper, and more environmental friendly than other methods. The performance of the electrolyte in carbonate-based solvents was tested to a half-cell lithium battery. Material characterizations were also performed to analyze the powder properties. Synthesized LiBOB was compared to commercial LiBOB to evaluate the basic properties as well as the electrochemical performance.

Experimental method

The materials used in this research were oxalic acid ($H_2C_2O_4.2H_2O$) with 98 % purity, lithium hydroxide (LiOH)

with 98 % purity, and boric acid (H_3BO_3) with 98 % purity, from Merck (Germany), mixed with molar ratio of 2:1:1 [8]. The lithium hydroxide has hygroscopic property; it binds water vapor in the atmosphere. Therefore, there was a heating step prior to the mixing step to release H_2O molecule within the compound. The heating treatment was performed at a temperature of 80 °C for 2 days. The materials were weighed and mixed using grinding mill until homogenous. Afterwards, the mixture was analyzed using differential thermal analyzer (DTA) [10] within temperature range of 30–500 °C, with the heating rate of 10 °C/min. Setaram TAG 24 was used for DTA analysis. The purpose of performing DTA analysis was to decide the heating temperature for preparing LiBOB. From DTA analysis, it was found that first heat preservation process was defined at a temperature of 120 °C retained for 4 h followed by heating at a temperature of 240 °C retained for 7 h [11]. LiBOB powder was milled before performing X-ray diffractometer (XRD) analysis using Rigaku Smartlab with CuKα as

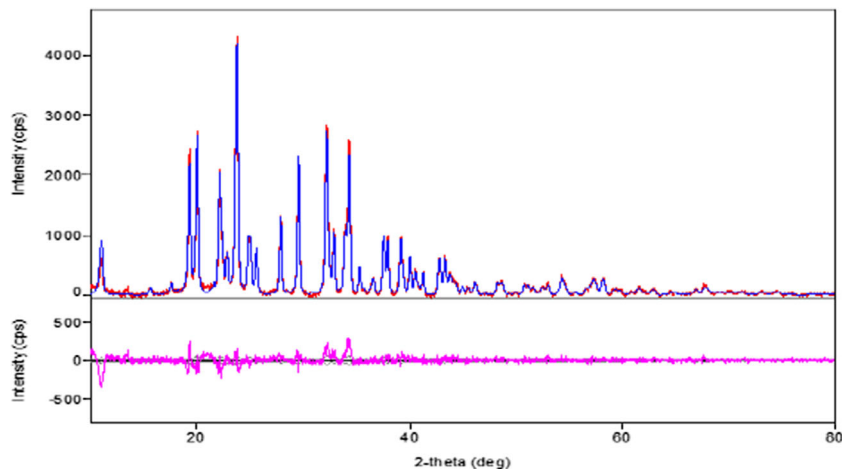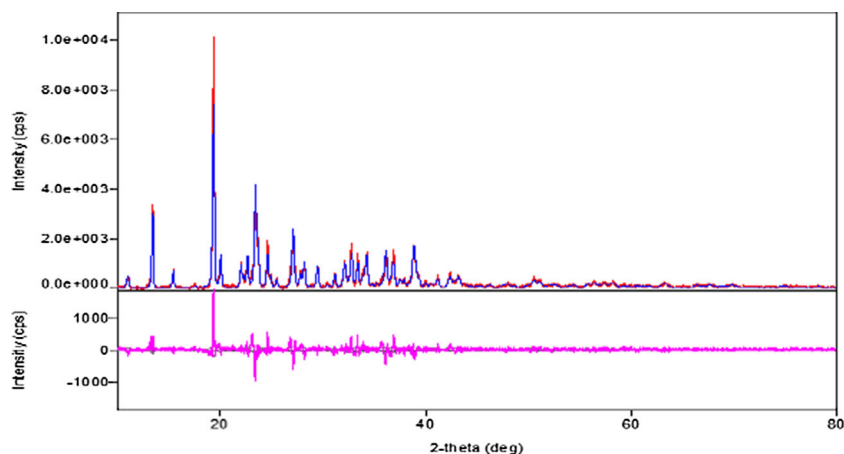Fig. 2 XRD refinement spectrum of synthesized LiBOB

Fig. 3 XRD refinement spectrum of commercial LiBOB

the target. XRD analysis resulted in a diffractogram describing diffraction peak, which was then analyzed with PDXL program to identify the phase formed in the sample, crystal structure as well as another crystallography data, and then compared to the XRD analysis result of commercial LiBOB (Sigma-Aldrich, Germany, analytical grade with purity of >99 %). LiBOB powder was also identified with Fourier transform infra red (FTIR) spectroscopy. Bruker-Tensor 27 was used for FTIR analysis, using KBR pellet method referring to ASTM E1252-07 test standard. Samples were made into pellets for analysis purpose, and the results were compared to those of commercial LiBOB. Subsequently, to know the microstructure and particle shape of the LiBOB powder, scanning electron microscope (SEM) analysis was conducted by Jeol JED 350 (Japan).

In order to synthesize liquid electrolyte, LiBOB was dissolved in ethylene carbonate, propylene carbonate, and dimethyl carbonate with 1:1:1 (v/v) at a concentration of 0.3, 0.5, and 0.7 M, respectively [12]. It was then tested on half-cells lithium battery, and the results were presented on cyclic voltammetry (CV) and charge-discharge (CD) curves.

Results and discussion

To identify the heating temperature on LiBOB synthesis, the mixture of the material, i.e., lithium hydroxide (LiOH), oxalic acid ($H_2C_2O_4 \cdot 2H_2O$), and boric acid (H_3BO_3), were analyzed using DTA. The result of the DTA in a form of thermogram-forming endothermic peaks showed the release of H_2O molecules and the reaction as well as the reduction of LiBOB-forming materials as illustrated in Fig. 1.

Peak 1 at 139.4 °C was the temperature when H_2O molecules were released from oxalic acid as well as oxalic lithium
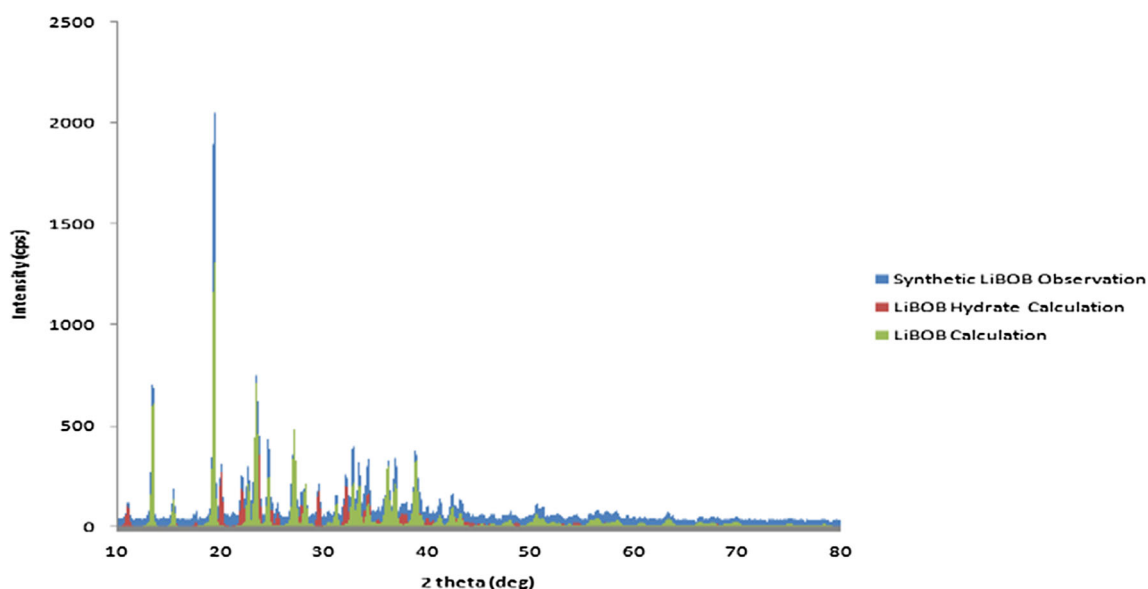

Fig. 4 The diffraction pattern of synthesized LiBOB matched with ICDD standards of LiBOB hydrate and LiBOB
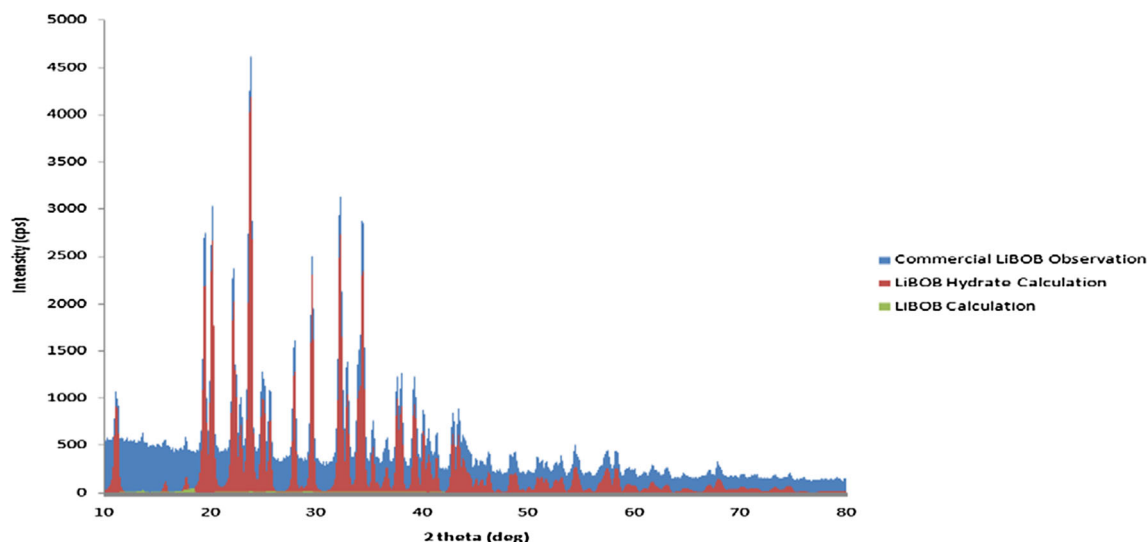
Fig. 5 The diffraction pattern of commercial LiBOB (P.A. grade) matched with ICDD standards of LiBOB Hydrate and LiBOB

hydrogen. HC_2O_4 $Li.H_2O$ would melt and release crystal water. The crystal water released would be as a medium which made the reactants contacted enough and reacted completely. Peak 2 at 172.2 °C appeared H_2O molecules were released from boric acid. Peak 3 at 247.9 °C was the formation reaction from the reactants into LiBOB. Peak 4 at 352.57 °C was the decomposition of LiBOB into oxalic lithium, B_2O_3, CO_2, and CO gas. Based on these analysis results, it was decided that the processes of preparing LiBOB by solid state reaction would be first heat preservation at 120 °C retained for 4 h and then heating at 240 °C retained for 7 h.

LiBOB powder as the result from synthesized was analyzed using XRD, and the result was compared with commercial LiBOB powder (Sigma-Aldrich, Germany), presented on Figs. 2 and 3, respectively.

In general, analytical grade commercial LiBOB consists of two phases, i.e., LiBOB and LiBOB hydrate. The ICDD standard for LiBOB and LiBOB hydrate phases has to be identified first before analyzing these two LiBOB samples using XRD as presented on Figs. 4 and 5. LiBOB has three strongest lines at 4.57621, 3.79991, and 3.29133 Å based on ICDD/PDF 4+ No. 00-062-0917. On the other hands, LiBOB hydrate has three strongest lines at 3.74141, 4.41409, and 4.57673 Å based on ICDD/PDF 4+ No. 01-073-9447, the three strongest line values

will be matched with indicated d-spacing values of the samples. The matching tolerances were ±0.01 for first d-spacing value and ±0.02 for second and third d-spacing values.

The diffraction pattern of synthesized LiBOB shows that there were also two indicated phases, LiBOB and LiBOB hydrate. The LiBOB phase was indicated by three d-spacing values, i.e., 4.5759, 3.7885, and 3.2899 Å, that matched with the ICDD standard of LiBOB (PDF 4+ No. 00-062-0917). The LiBOB hydrate phase was indicated by three d-spacing values, i.e., 3.7578, 4.426, and 4.5759 Å that matched with the ICDD standard of LiBOB hydrate (PDF 4+ No. 01-073-9447). The refinement was done by the Rietveld analysis method using PDXL software. The reliability factor Rwp is 17.61 % and chi^2 is 2.1565. The lattice parameters of this sample after refinement are shown in Table 1. The RIR-method quantitative analysis using PDXL software shows that synthesized LiBOB consists of 36.1 wt% LiBOB hydrate and 63.9 wt% LiBOB.

The diffraction pattern of commercial LiBOB shows that there were two indicated phases that was LiBOB and LiBOB hydrate. The LiBOB phase was indicated by three d-spacing values, i.e., 4.5852, 3.778, and 3.28381 Å, that matched with ICDD standard of LiBOB (PDF 4+ No. 00-062-0917). The LiBOB hydrate phase was indicated by three d-spacing value,

Table 1 Crystallographic data of synthesized LiBOB sample from Rietveld refinement

Indicated phases	Lattice parameter and unit cell volume				Lattice system	Space group	Density
	a/Å	b/Å	c/Å	V/Å^3			(g/cm3)
LiBOB hydrate	16.134	15.928	5.6183	1443.8	Orthorhombic	Pbca	1.939
LiBOB	6.3657	7.5844	13.172	635.92	Orthorhombic	Pnma	2.021

Table 2 Crystallographic data of commercial LiBOB sample from Rietveld refinement

Indicated phases	Lattice parameter and unit cell volume				Lattice system	Space group	Density
	a/Å	b/Å	c/Å	V/Å^3			(g/cm3)
LiBOB Hydrate	16.118	15.915	5.6145	1440.2	Orthorhombic	Pbca	1.966
LiBOB	7.27	6.87	13.06	652	Orthorhombic	Pnma	2.060

i.e., 3.74141, 4.4253, and 4.5852 Å, that matched with ICDD standard of LiBOB hydrate (PDF 4+ No. 01-073-9447). The refinement was done by the Rietveld analysis method using PDXL software. The reliability factor Rwp was 8.19 % and chi^2 was 2.8826. The lattice parameters of this sample after refinement are shown in Table 2. The RIR-method quantitative analysis using PDXL software shows that commercial LiBOB consists of 97.3 wt% LiBOB hydrate and 2.7 wt% LiBOB.

Both samples indicated two phases, LiBOB and LiBOB hydrate. LiBOB hydrate was the dominant phase of commercial LiBOB. However, the synthesized LiBOB has more LiBOB phase than commercial LiBOB, i.e., 63.9 wt%. The difference of these compositions could make some effect in solubility and electrochemical performance of these two electrolyte samples. FTIR analysis (identifying OH bond) is needed for comparing hydrate indicated from LiBOB hydrate phase based on XRD analysis. CV and CD tests were needed to see the effect of hydrate from LiBOB hydrate phase to electrochemical performance of these electrolytes.

From FTIR analysis, infrared spectrum within the wave number range of 500–4000 cm^{-1} was obtained and shown in Fig. 6. From this infrared spectrum data, the functional groups in the LiBOB powder could be identified. The vibration likelihood might happen here were the functional group of C-O, C=O, B-O, O-B-O, and C-C which are alkyl group, carbon group, etc. The wave number of 1768–1808 cm^{-1} represented vibration of C=O, while 994–1303 cm^{-1} was the vibration of C-O-B-O-C. The wave number of 712 cm^{-1} was a typical peak of COO deformation. Based on the reference, the absorption bands that should appear for $LiB(C_2O_4)_2$ or LiBOB compound were at 1372, 1087, and 860 cm^{-1} [13]. There was a slight difference between synthesized and commercial LiBOB to the typical LiBOB wave numbers from the reference. For the reference LiBOB compound [14], there was a stretching of C=O and B-O at wave number 1750 and 1372 cm^{-1}, respectively, and asymetric stretching of C-O-C at wave number 1008 cm^{-1}. While those wave numbers did not appear at synthesized LiBOB, there was an absorption band O-B-O at wave number 1081 cm^{-1} that was the typical peak of a LiBOB compound—which at reference LiBOB is shown at wave number 1070 cm^{-1}. The absorption bands at 3513 cm^{-1} at both synthesized and commercial LiBOB indicates OH bond, which signifies that there was a possibility of imperfect reaction of $B(OH)_3$ or $(CO_2H_2)_2$ compound. It was also possible that it binded OH from the air because of the hygroscopic properties of LiBOB. The binding of OH group from the air by LiBOB was forming LiBOB hydrate; this agrees with the XRD analysis results which showed LiBOB hydrate phase. From FTIR spectrum profile as shown at Fig. 6, there was no
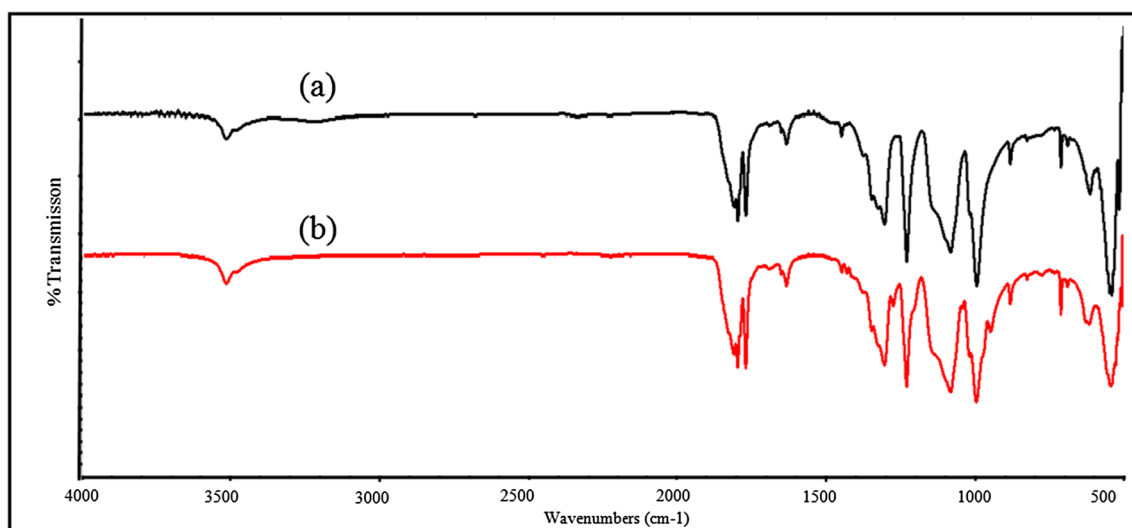

Fig. 6 FTIR spectrum of **a** synthesized LiBOB and **b** commercial LiBOB

Fig. 7 SEM results of **a** synthesized LiBOB and **b** commercial LiBOB

(a)   (b)

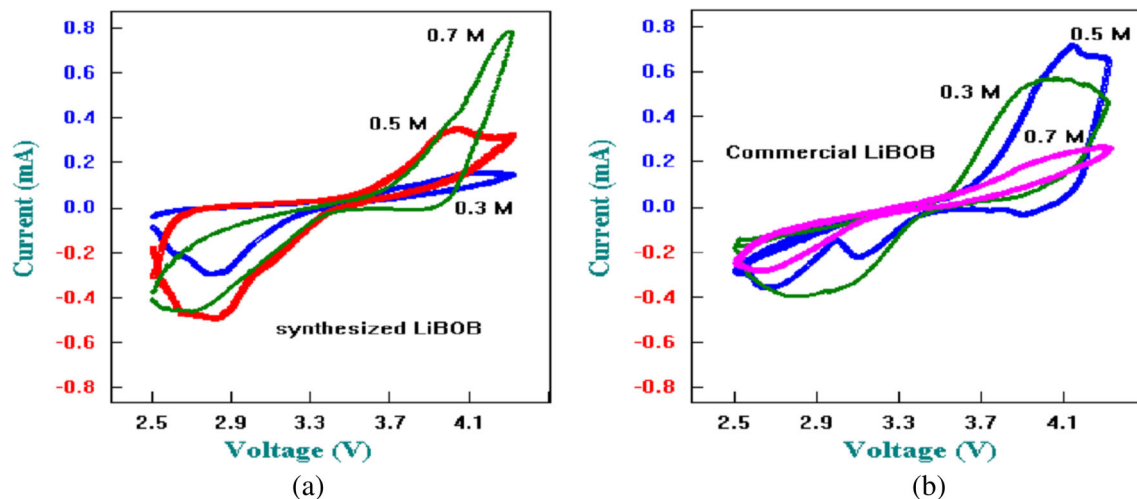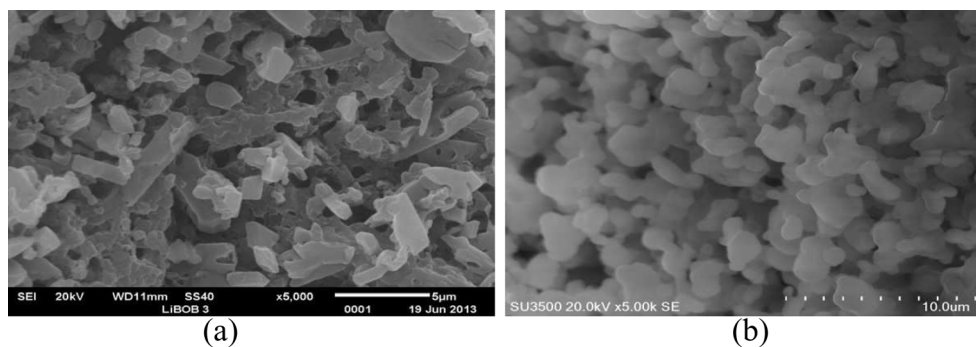(a)   (b)

Fig. 8 Cyclic voltammetry curve of half-cells with electrolyte **a** synthesized LiBOB and **b** commercial LiBOB

significant differences from commercial LiBOB compared to synthesized LiBOB.

SEM analysis results of synthesized and commercial LiBOB sample is shown on Fig. 7a, b, respectively. It can be seen that the particles are in spherical and cylindrical shape.

The morphological shape of synthesized LiBOB is not as well-ordered as the uniformly shaped commercial LiBOB. This was probably caused by a grinding process and particle separation of commercial LiBOB. In this research, the grinding process was done manually with a pestle and mortar. It
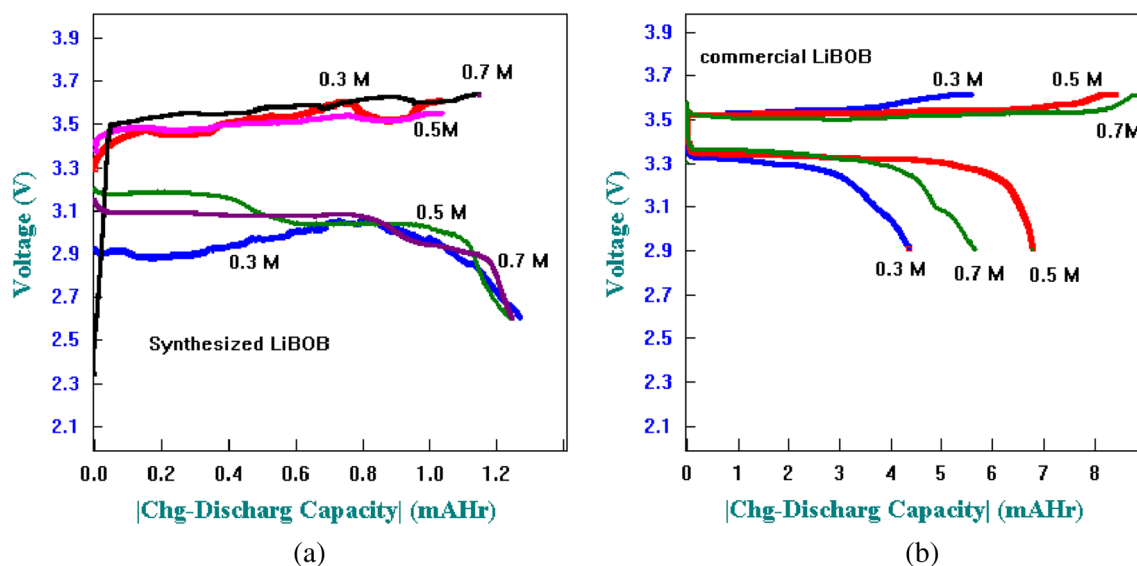

(a)   (b)

Fig. 9 Charge-discharge curve of half-cells lithium-ion battery with electrolyte **a** synthesized LiBOB and **b** commercial LiBOB

was also observed during the mixing process of liquid electrolyte that synthesized LiBOB was less soluble than commercial LiBOB, as was seen from the deposit of undissolved powder in carbonate solvent. This was possible because of synthesized LiBOB have lower performance than commercial LiBOB as seen in CV curves presented in Fig. 8.

The test results of LiBOB electrolyte exposed to half-cells lithium battery are presented on CV curves in Fig. 8. The cell used LiFePO$_4$ as cathode, metal lithium as anode, and LiBOB electrolyte with concentrations of 0.3, 0.5, and 0.7 M. These figures indicated that synthesized LiBOB was already functional to use in half-cells lithium battery, despite of the relatively lower current compared to commercial LiBOB.

The CV curve on Fig. 8 was taken from the best performance of each sample during the test cycle. Figure 8a, b showed that the optimum concentration for LiBOB electrolyte for half-cells application was at 0.5 M concentration. Similar series of experiments were conducted to explore electrochemical behavior of synthesized LiBOB for different concentrations, i.e., 0.3, 0.5, and 0.7 M. The result of the cyclic voltammetry test was presented on Fig. 8a. The experiment result for synthesized LiBOB showed agreement with the commercial one: optimum performance of the battery at 0.5 M concentration. Beside cyclic voltammetry, we also tested the battery by exposing it into a charge and discharge process to see the maximum capacity through voltage exposure. The CD curve of synthesized and commercial LiBOB is presented on Fig. 9a, b, respectively.

The above charge-discharge curve was taken from the first cycle of the half-cell battery. From Fig. 9a can be seen LiBOB synthesis capacity of 1.2 mAh or approximately 1/4 times the capacity of commercial LiBOB. Figure 9b showed that 0.5 M concentration had the best performance during the charge and discharge cycle, then 0.7 M concentration, and the last one was 0.3 M. Commercial LiBOB with 0.7 M concentration has higher maximum charge capacity compared to 0.5 M commercial LiBOB, but the discharge capacity of 0.7 M concentration was lower than 0.5 M concentration. It means that columbic efficiency of 0.5 M concentration was better than 0.7 M.

These results indicate synthesized LiBOB capacity is lower than commercial LiBOB capacity due to differences in particle morphology LiBOB. SEM information shows granular particles have a characteristic porous commercial LiBOB so it has better solubility of synthesized LiBOB.

As for the synthesized LiBOB, all concentrations have almost similar capacity but compared with LiBOB commercial, their capacity only reached 1/4 times. Sample with 0.5 M concentration has the lowest charging voltage, followed by 0.3 and 0.7 M for the highest charging voltage. It means that synthesized LiBOB at 0.5 M was the least consuming energy at charging condition. From discharging voltage plateau, it was seen that the sample with 0.3 M concentration has the lowest discharging voltage, followed by 0.7 and 0.5 M concentrations for the highest discharging voltage. Even though the discharge capacity seemed similar for the three samples, the discharging voltage plateau for the sample with 0.3 M concentration was the lowest. It can be concluded that highest withdrawn energy was from the sample with 0.5 M concentration.

Conclusion

The obtained XRD analysis results of synthesized LiBOB showed a similar pattern with commercial LiBOB. The phases formed were LiBOB and LiBOB hydrate, with orthorombic crystal structure. FTIR spectroscopy analysis results yielded the formation of functional groups of LiB(C$_2$O$_4$)$_2$ compound which is characterized by the appearance of absorption bands of C-O, C=O, B-O, O-B-O, and C-C. SEM analysis showed that the particle morphology of synthesized LiBOB produced was still not uniform. Half-cell test of LiBOB as battery electrolyte is shown on the CV and CD curve. Overall performance of synthesized LiBOB as liquid electrolyte in half-cell lithium battery was still lower than commercial LiBOB. A possible explanation for this could be the less uniform particle morphology and less soluble powder in carbonate solvent. Further study in LiBOB particle morphology and solubility needs to be performed to increase the performance of LiBOB as an electrolyte in lithium-ion battery.

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