

A Guide to Water Free Lithium Bis(oxalate) Borate (LiBOB)

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ABSTRACT: Lithium bis(oxalate)borate, $\text{Li}(\text{C}_2\text{O}_4)_2$ (LiBOB), is one of the most important electrolyte additives for Li-ion batteries (LIBs) due to its numerous advantages such as thermal stability, good solubility in organic solvents, high conductivity, and low cost as well as providing safer operations with superior electrochemical performance compared to conventional electrolyte combinations. However, the use of LiBOB is limited due to slight instability issues under ambient conditions that might require extra purification steps and might result in poorer performances in real systems. Here, we address some of these issues and report the high purity water free LiBOB synthesized with fewer processing steps employing lithium carbonate, oxalic acid, and boric acid as low-cost starting materials, and via ceramic processing methods under protective atmosphere. The physical and chemical characterizations of both anhydrous and monohydrate phases are performed with X-ray powder diffraction (XRPD), Fourier-transform infra-red spectroscopy (FTIR), Raman spectroscopy and scanning electron microscopy (SEM) analyses to determine the degree of the purity and the formation of impurities like $\text{LiBOB}\cdot\text{H}_2\text{O}$, HBO_2 and $\text{Li}_2\text{C}_2\text{O}_4$ as a result of the aging investigations performed. Differential thermal analysis (DTA) is applied to determine the optimum synthesis conditions for anhydrous LiBOB and to analyze the water loss and the decomposition of $\text{LiBOB}\cdot\text{H}_2\text{O}$. Aging experiments with the water free LiBOB are carried out to evaluate the effect of humidity in the phase changes and resulting impurities under various conditions. The detrimental effect of even slightest humidity conditions is shown, and protective measures during and after the synthesis of LiBOB are discussed. Anhydrous LiBOB could be widely used as an electrolyte additive to improve the overall electrochemical performances for LIBs through development of a protective solid electrolyte interphase (SEI) on the surface of high voltage cathodes and bringing about superior electrochemical properties with increased cycling stability, rate capability and coulombic efficiency, if synthesized, purified, and handled properly before use in real electrochemical systems.

KEYWORDS: *Li-ion batteries, LiBOB, humidity, electrolyte, additive*

1. INTRODUCTION

Electrolyte salts and additives play a crucial role in increasing the cycle life, capacity and safety of batteries especially for high voltage applications¹⁻³. Lithium bis(oxalate) borate, $\text{LiB}(\text{C}_2\text{O}_4)_2$ (LiBOB), is one of the most widely used electrolyte additives in Li-ion batteries (LIBs) and has a potential to be an alternative of the commercially used lithium hexafluorophosphate (LiPF_6) as an electrolyte salt when dissolved in suitable solvents. LiBOB provides electrochemical stability at high applied potentials and high thermal stability under different electrochemical conditions⁴⁻⁶. LiBOB also promotes the formation of a protective solid-electrolyte interface (SEI) layer; thus increasing capacity and cycle life when used as an electrolyte additive⁷⁻¹⁴.

LiBOB can address the need for stable electrolyte compositions for high voltage cathode materials and applications. In a mixed solvent system (γ -butyrolactone and dimethyl carbonate), it was shown that LiBOB provides oxidative stability up to 5.3 V in Li-ion batteries^{3, 15}, whereas LiPF_6 can be only employed up to 4.5 V. The thermal stability of bulk LiPF_6 is 80 °C, and it is safe to use up to 50 °C in LIBs. Additionally, at higher temperatures, LiPF_6 is susceptible to decompose into LiF and PF_5 resulting in low electrochemical performances and safety issues^{8, 16}. On the other hand, bulk LiBOB decomposes at 300 °C and it is stable up to 70 °C in LIBs¹⁷. There are several other reports where LiBOB enables a stable operation at voltages higher than 4.5 V¹⁸⁻²⁰. Besides, LiBOB provides safer operation for Li-ion batteries not only due to its high thermal stability but also due to the protective SEI formation. SEI layer formation does not only play an active role only in the first cycle in the battery; yet, SEI keeps growing and changing with processes such as dissolution and precipitation^{21, 22}. Thus, understanding the SEI chemistry and stabilizing the SEI are important challenges in the development of long-life and safe LIBs, as well.

Other common Li-ion battery salts such as LiPF_6 , LiAsF_6 , and LiClO_4 were shown to decompose to form corrosive and reactive chemicals²³. The high oxidation state of Cl(VII) in LiClO_4 causes reactions with a range of organic solvents²⁴, and As(III) and As(0) that form during redox reactions involving LiAsF_6 are toxic²⁵, and LiTf based electrolytes are highly corrosive²³. On the other hand, LiBOB has received great interest owing to its superior properties such as thermal stability, good solubility in organic solvents, improved cycling stability with high voltage

cathodes, environmentally friendliness, and low cost^{9, 11, 14, 26, 27}. LiBOB was also shown to protect graphite anodes from exfoliation in PC-based electrolytes and to develop a SEI on the surface of carbon based cathode materials⁶. Additionally, corrosive and dangerous by-products such as HF do not evolve upon cycling when LiBOB is used instead of LiPF_6 . Unlike LiPF_6 and other salts such as LiClO_4 , LiAsF_6 and LiTf, LiBOB directly forms a protective SEI independent of the carbonate electrolyte solvent employed. Additionally, other potentially corrosive and dangerous by-products such as PF_5 and LiF do not evolve upon cycling when LiBOB is used²⁸⁻³⁰. If the applications of LiBOB as an additive are considered, Pieczonka et al. observed that the addition of 1 wt.% LiBOB in traditional electrolytes increases the cycling stability and coulombic efficiency for a high voltage spinel/graphite battery system, and the addition of 3 wt.% LiBOB eliminated the PF_5 decreasing the Mn dissolution from the $\text{Li}_{1-x}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{Mn}_{1.5}\text{O}_4$ (LNFMO) cathode¹⁹. In another study, Lee and coworkers employed LiBOB as an electrolyte additive to develop a protective SEI for high potential $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Mn}_{1.5}\text{Co}_{0.17}\text{O}_2$ cathodes improving the cycling stability and rate capability via eliminating the electrolyte decomposition³¹.

Although LiBOB is a very promising electrolyte salt and additive for Li-ion batteries, up to date, there are only few reports³²⁻³⁴ investigating different synthetic routes. LiBOB is mainly synthesized using high-cost lithium salts such as LiBH_4 and LiOH in most of the current reports^{32, 33, 35}. In addition, to the best of our knowledge, $\text{LiBOB}\cdot\text{H}_2\text{O}$ is present as a by-product in all reported LiBOB synthesis methods in the literature. Depending on the reactants used in LiBOB synthesis, impurities such as lithium oxalate and lithium carbonate were also detected in the final product. In addition, there is a lack of research focusing on the stability of this important electrolyte salt and additive under humidity during and after the synthesis, and under prolonged air exposure. Therefore, herein, we focus on these issues and report on the importance of new synthetic routes and humidity conditions to obtain a high purity water free LiBOB. We synthesize anhydrous and higher purity LiBOB using low cost starting materials and fewer processing steps compared to most prevalent synthesis methods in the literature. Avoiding moisture and impurities in LiBOB and such electrolyte salts are vital for the performance of LIBs. Thus, we also underline the importance of synthesizing and employing LiBOB under protective atmosphere to eliminate hydrous phase and impurity

formation by investigating the aging results of the synthesized high purity salt under atmospheric conditions.

2. EXPERIMENTAL SECTION

2.1 Synthesis of anhydrous LiBOB

LiBOB is synthesized using lithium carbonate (Li_2CO_3 , $\geq 99\%$, Alfa Aesar), oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$, $\geq 98\%$, Alfa Aesar), and boric acid (H_3BO_3 , $\geq 99\%$, Alfa Aesar) as starting materials. Stoichiometric amounts of the compounds (following the equation in **Figure 1d**) are mixed and ground in a mortar. Excess amount of deionized water is added to the powder mixture, and the mixture is stirred continuously at 80°C under ambient conditions until all water is evaporated. A pellet made from this powder precursor is placed in a glassy carbon boat and covered/protected with the same precursor powder. Then, the reaction boat is placed in a quartz tube within a horizontal tubular furnace, and the reaction is carried under protective atmosphere (Ar, N_2 or dry air) at 250°C for 10-15 hours. The products are transferred into an Ar glovebox (O_2 and $\text{H}_2\text{O} < 1$ ppm) without exposure to ambient atmosphere. After the synthesis, the protective powder is discarded, and the anhydrous LiBOB pellet is ground in a mortar in the glovebox. Aging of the anhydrous LiBOB powder is done under ambient conditions (at RT, and 70 % Average Relative Humidity). 2-3 grams of LiBOB powder is placed in semi-closed autoclave bottles and left in fume hoods with ventilation for 5, 15, 30 minutes, and 2 days.

2.2 Characterization of LiBOB

The phase and purity of the samples are determined by X-ray powder diffraction (XRPD) method using a Bruker D8 Advance X-ray diffractometer, and $\text{Cu K}_{\alpha 1}$ radiation (operated at 40 mA, 40 kV). The purity of the as synthesized LiBOB and impurities forming upon aging are further characterized by vibrational spectroscopy analyses. Fourier-transform infra-red spectroscopy (FTIR) is performed on a Thermo Scientific Nicolet iS10 spectrometer with a single reflection diamond attenuated total reflectance (ATR) module, and Renishaw inVia Raman microscope equipped with a 532 nm laser as the excitation source is used to perform Raman spectroscopy. The morphology of the as synthesized and aged powders is investigated by

scanning electron microscopy (SEM) analysis using a Zeiss Ultra Plus field emission GeminiSEM. Differential thermal analysis (DTA) is utilized to monitor the reaction and any exothermic and endothermic reactions in the selected temperature range using a Netzsch STA 449 thermal analysis system.

3. RESULTS AND DISCUSSION

LiBOB is synthesized in high purity following the procedure depicted in **Figure 1a and 1b**. The phase and purity of as-synthesized LiBOB is investigated via XRPD analysis by comparing the experimental reflection pattern with the calculated reflection pattern of LiBOB (ICSD 281623) (**Figure 1c**). The XRPD pattern of the as-synthesized LiBOB match the theoretical pattern, and the reflections belong only to anhydrous LiBOB³⁶. This finding shows that single phase anhydrous LiBOB could be obtained in a single synthetic step without the need of any extra recrystallization steps to eliminate $\text{LiBOB}\cdot\text{H}_2\text{O}$. The lack of any other reflections belonging to possible impurity phases shows that they are under ~ 1 wt-%. Most importantly, $\text{LiBOB}\cdot\text{H}_2\text{O}$ which is the main impurity in the synthesis that could also cause parasitic reactions in LIBs is not observed. Key points in achieving high purity anhydrous LiBOB with the experimental design were conducting the reaction under inert atmosphere (under argon, nitrogen, and dry air) and protecting the pellet with the precursor powder following well-known ceramic processing methods (**Figure 1a, Figure 1c and Figure S1**).

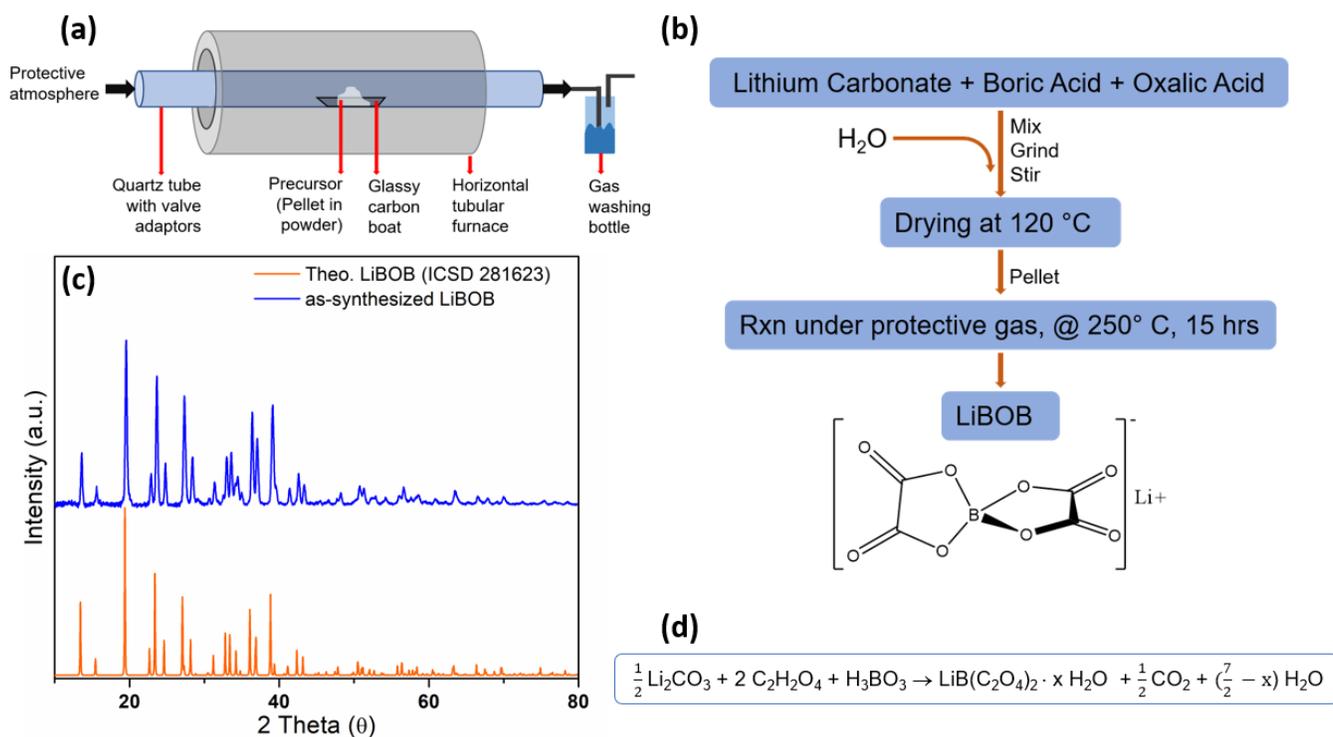


Figure 1. (a) A schematic representation of the experimental setup for high purity anhydrous LiBOB synthesis. Ar, N₂ and dry air are employed as protective gases (please see Supplementary Figure S1 for the N₂ and dry air synthesis results). (b) Processing steps used in the synthesis of high purity anhydrous LiBOB. (c) XRPD patterns of theoretical LiBOB (ICSD 281623)³⁶ (orange) and as-synthesized LiBOB (blue). Reflections belonging only to LiBOB are observed in the XRPD pattern for the synthesized sample. (d) The overall chemical equation for the LiBOB synthesis reaction.

The reaction of the precursor pellet was monitored via differential thermal analysis (DTA), and different synthesis conditions were also carried out at varied temperatures to determine the optimum temperature window for the high purity LiBOB synthesis (**Figure 2**). From the XRPD analysis and DTA data, 225 - 300 °C temperature range could be claimed to be the optimum range for this synthesis. The XRPD and DTA findings show that anhydrous LiBOB decompose into lithium oxalate (Li₂C₂O₄) and other amorphous phases at temperatures ca. > 315 °C and at temperatures below 250 °C either monohydrate phase is observed or the reaction is not complete (**Figure 2a**). According to the Reference intensity ratio (RIR) method³⁷⁻³⁹, the percentage of anhydrous LiBOB for as-synthesized samples at 200 °C, and 250 °C was found ~ 95 wt-% and ~ 99.0 wt-%, respectively. Humidity and impurities in LiBOB have detrimental effects on the performance of Li-ion batteries⁴⁰, and although it was claimed that monohydrate of LiBOB is stable⁴¹, we show that hydrated LiBOB could decompose into

HBO₂, Li₂C₂O₄ when exposed to air (**Figure S2**). The presence of such impurities in electrolyte solution could cause capacity fading and safety problems under extensive cycling.

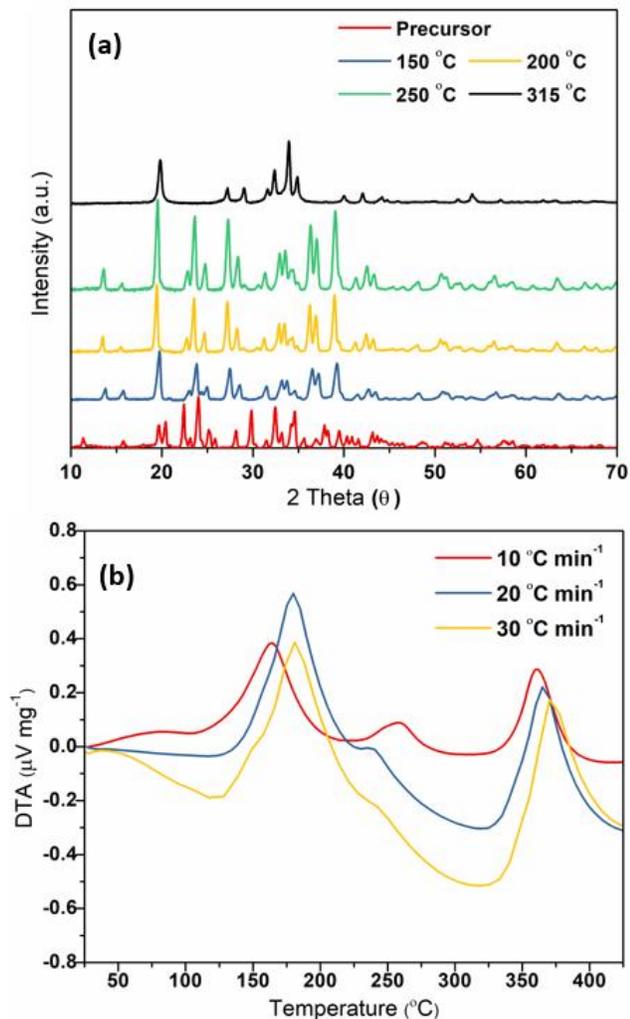


Figure 2. (a) XRPD patterns for the precursor and samples synthesized at 150 °C (blue), 200 °C (yellow), 250 °C (green) and 315 °C (black). (b) DTA data taken at different heating rates showing the reaction temperature for LiBOB synthesis and decomposition temperature of the synthesized LiBOB.

Scanning electron microscopy (SEM) was employed to further understand the particle morphologies and the effect of humidity on those. A homogeneous distribution of particles is observed in SEM images for the samples calcined at temperatures between 250 - 300 °C (**Figure 3a, c, d**). These anhydrous LiBOB particles are few microns in size and prism shaped, whereas synthesis at lower temperatures (< 150 °C) and the product after prolonged air exposure yield rumbled morphologies without any well-defined structures. (**Figure 3b, Figure S4**). The detrimental

effect of humidity on high purity LiBOB can be easily observed via SEM analysis, as well (**Figure S3**). The morphology of the anhydrous LiBOB particles start changing after ≤ 5 -minute-long exposure to air, and curvatures and pores start to form on the surface of prisms (**Figure S3**).

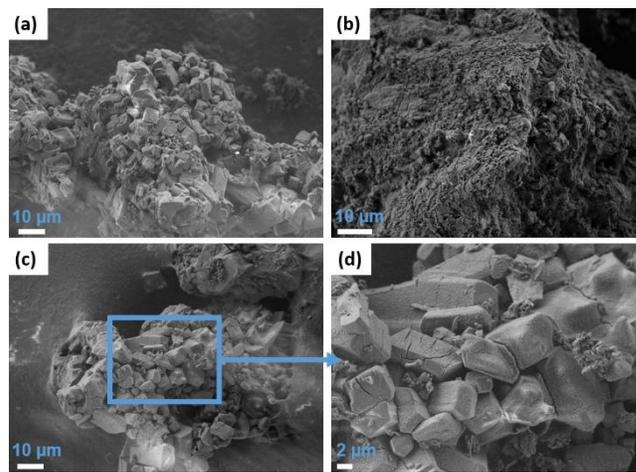


Figure 3. (a), (c) SEM micrographs showing the particle size and morphology of anhydrous LiBOB synthesized at 250 °C. (b) Morphology of the products synthesized at 150 °C. (d) Magnified region from c, displaying LiBOB crystals.

In order to analyze the effect of prolonged air exposure to this important electrolyte additive, and to further investigate the influence of humidity in phase changes, aging experiments were performed. Aging of the anhydrous LiBOB powder was done under ambient conditions (at RT (~ 25 °C), and 70 % Average Relative Humidity) for 5, 15, 30 minutes and 2 days. The effect of humidity is first investigated through XRPD analysis. XRPD powder patterns in **Figure 4a** show that as-synthesized powder consists of only anhydrous LiBOB phase, and ~ 42 wt-% monohydrate phase ($\text{LiBOB}\cdot\text{H}_2\text{O}$) forms after 5 minutes of aging under given conditions according to the RIR method. After only 15 minutes of exposure to air under given conditions, almost all of the anhydrous LiBOB turns into $\text{LiBOB}\cdot\text{H}_2\text{O}$, and the complete hydration occurs after 30 minutes of aging (**Figure 4a & 4b**). The presence of water in the structure can be further confirmed by DTA analysis (**Figure 4c**). The structural water is given from the monohydrate phase at ~ 150 °C, and the phase decomposition into $\text{Li}_2\text{C}_2\text{O}_4$ and other amorphous phases start at ~ 315 °C. These findings signify the importance of synthesizing and preserving LiBOB under protective atmos-

phere. Since purity of electrolyte salts and additives play a crucial role in the cycle life and safety of LIBs⁴², the measures taken here in the synthesis of LiBOB can be considered as critical necessary steps.

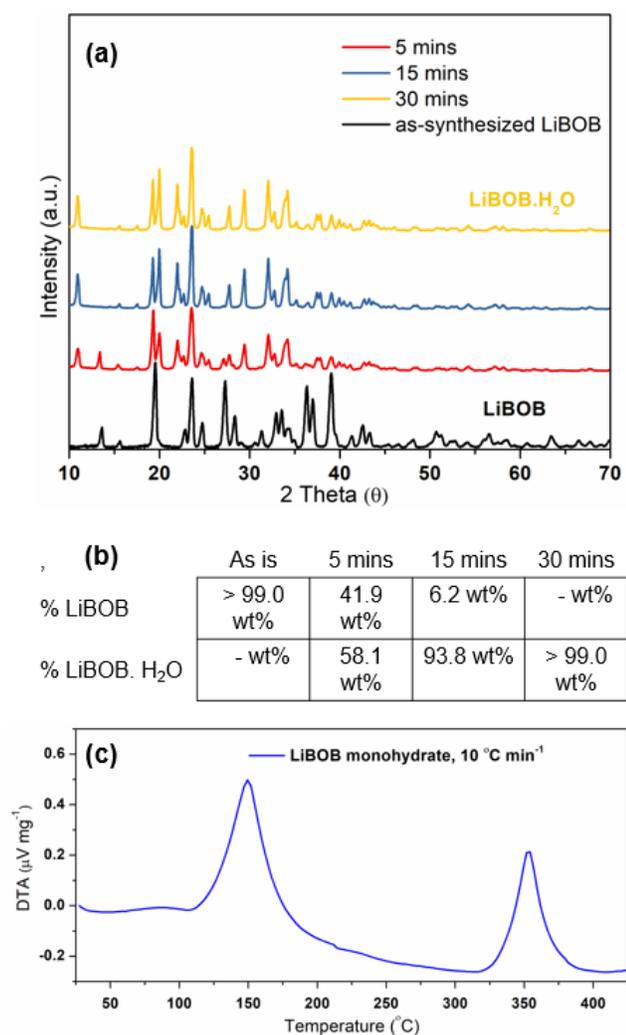


Figure 4. (a) XRPD patterns of the as-synthesized and aged (5, 15, and 30 minutes) LiBOB samples. (b) Phase composition of LiBOB and LiBOB.H₂O in as-synthesized and aged samples calculated via reference intensity ratio (RIR) method. (c) DTA analysis showing the water loss and decomposition of LiBOB.H₂O.

The vibrational spectroscopy analysis is in good agreement with XRPD and DTA analyses in terms of confirming the high purity LiBOB phase after the synthesis, and verifies the humidity effect after aging. Both Raman and FTIR spectra of the as-synthesized phase clearly show the high purity of the as-prepared

LiBOB after the synthesis^{10, 40, 43} and no major impurity phases are observed (**Figure 5a & Figure 5b**). In the FTIR spectrum (**Figure 5b**) of the LiBOB phase, the strong absorption peak at 1765-1825 cm⁻¹ could be assigned to the stretching vibrations of C=O bond, whereas the region of 980-1370 cm⁻¹ is attributed to the C-O and B-O stretching modes^{10, 32}. To analyze the hydration of the anhydrous phase, the FTIR spectra from the aged LiBOB samples were also collected. The water absorption peak intensity at ca. 3500 cm⁻¹ increases with the aging time, and several absorption peaks in the range of 1500-800 cm⁻¹ shift-change due to the structural deterioration of LiBOB^{40, 44}. It should be also noted that a very small water peak might be visible in the spectrum of the as-synthesized sample, since the measurement was not done in a protective atmosphere, so the sample was exposed to air for a minute. As the aging time increases, it is also evident that there is Li₂C₂O₄ formation in samples with the observation of small intensity peaks at 1658 and 778 cm⁻¹^{40, 45}. These findings are also consistent with XRPD patterns of the aged LiBOB for two days and the decomposed LiBOB (**Figure S2, Figure 2a-315 °C** pattern). As shown in the **Figure S2**, in addition to the diffraction pattern of the LiBOB.H₂O, reflections at 20.08° and 27.88° could be attributed to the formation of HBO₂, and reflections at 22.06° and 29.48° indicate the presence of Li₂C₂O₄, as similarly observed by other investigators^{33, 46}.

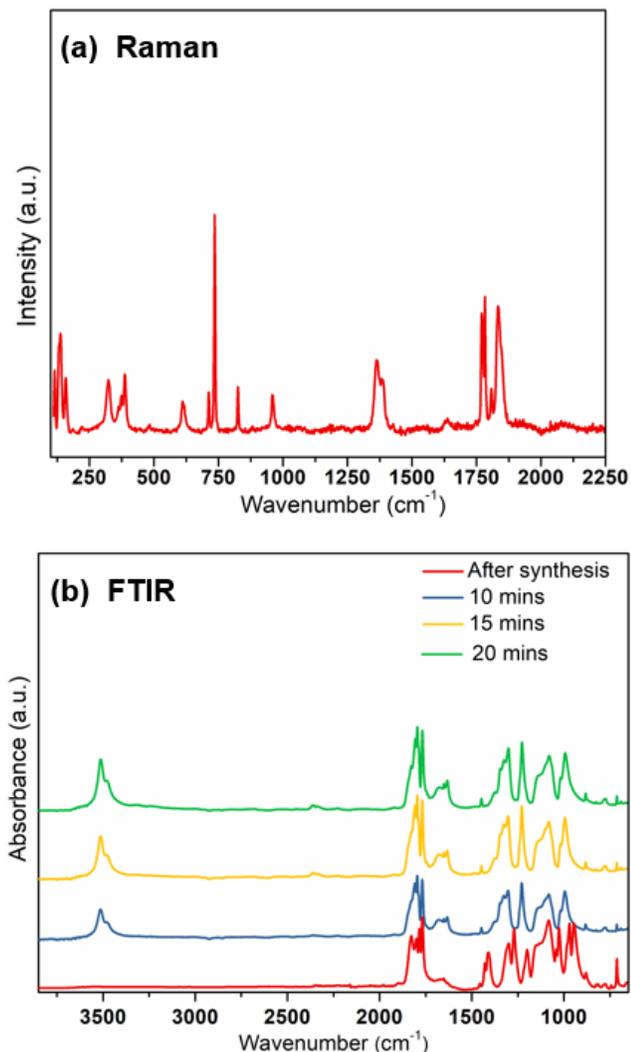


Figure 5. (a) Raman spectra of anhydrous LiBOB. (b) FTIR spectra of as synthesized and aged LiBOB showing the formation of monohydrate phase and secondary phases upon exposure to ambient conditions.

To sum up, the detrimental effect of humidity during and after the synthesis of LiBOB is evident with the monohydrate phase formation that could further decompose mainly into $\text{Li}_2\text{C}_2\text{O}_4$ and amorphous other phases. These impurities could of course be eliminated through repeated recrystallization steps with polar aprotic organic solvents, but this would bring about additional complications, such as cost increases and environmental burden with the use of organic solvents. Therefore, high purity synthesis of anhydrous LiBOB with least possible steps is very important, and would decrease the number of recrystallization steps in case if they are needed. The employment and

widespread application of LiBOB as an electrolyte additive in LIBs could be considered as limited in the current state-of-art. Yet, we think that this limitation is also present because of the unexpected or low quality results obtained due to the occurrence of impurities and hydrated phases^{40-42, 47}. This occurrence and impurities may not even be realized by the unsuspecting, as they are very easy to form as we have shown here. Nevertheless, with the proper use, LiBOB could be expected to bring superior electrochemical performances when it is used as an electrolyte additive for LIBs including cycling stability, rate capability, energy density and coulombic efficiency by preventing the electrolyte decomposition and the formation of dangerous byproducts. Additionally, a protective LiBOB-derived SEI will develop on the electrode surface enhancing the interfacial stability for high temperature operations.

4. CONCLUSIONS

LiBOB was synthesized under protective atmosphere using lithium carbonate, oxalic acid, and boric acid as low-cost starting materials by applying ceramic processing methods to achieve a high purity product. Aging investigations were also carried out to further evaluate the effect of humidity and the formation of $\text{LiBOB}\cdot\text{H}_2\text{O}$ and impurities such as HBO_2 , $\text{Li}_2\text{C}_2\text{O}_4$ that are undesirable in applications for high performance LIBs. According to the DTA results, the synthesis temperatures above 315°C cause decomposition of anhydrous LiBOB into impurities and at temperatures below 200°C the formation of the monohydrate phase may result in the capacity fade and poor cycling performance for LIBs. As shown from the XPRD data and FTIR and Raman spectra, the resulting salt is anhydrous and high purity over ~ 99 wt-%; thus, a higher purity is obtained with fewer and practical processing steps compared to some commercial products and LiBOB reported in the literature. XPRD analysis showed that ~ 42 wt-% monohydrate phase ($\text{LiBOB}\cdot\text{H}_2\text{O}$) formed only after 5 minutes of aging at RT-70 % relative humidity, and only after 30 minutes of exposure to air under given conditions, the complete hydration occurred. From the SEM micrographs, consistent with the findings from XPRD and FTIR, the structural deterioration of LiBOB can also be tracked. The longer exposures in the time scale of days further decomposed $\text{LiBOB}\cdot\text{H}_2\text{O}$ into other impurity phases, mainly $\text{Li}_2\text{C}_2\text{O}_4$. Keeping the purity high and avoiding exposure to humidity in all pro-

cessing steps are crucial for stable performance of batteries using LiBOB either as an electrolyte salt or additive and towards widespread applications, especially high voltage LIBs.

5. ASSOCIATED CONTENT

Supporting Information

XRPD patterns of high purity anhydrous LiBOB synthesized using different protective gases i.e. under dry air and N₂ atmosphere. XRPD pattern showing crystalline water, HBO₂, Li₂C₂O₄ formation after aging anhydrous LiBOB for 2 days under ambient conditions. SEM Micrographs for anhydrous LiBOB ages under ambient conditions showing changes in the prismatic morphology and formation of pores. SEM Micrographs showing the morphology of the products synthesized at 150-200 °C.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

ACKNOWLEDGMENTS

This study was financially supported by the National Boron Research Institute (BOREN), (No. 2018-31-07-15-003). Yaprak Subaşı thanks BOREN for funding her scholarship. The authors thank Koç University Surface Science and Technology Center (KUYTAM) and Koç University Boron and Advanced Materials Application and Research Center (KUBAM) for the use of characterization facilities.

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