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Synthesis of LiBOB Fine Powder to Increase Solubility

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Abstract

Lithium bis (oxalate) borate or LiBOB compound has captured interest of researchers, because it is potentially viable to be used as electrolyte salt in lithium-ion battery system. This compound is easy to synthesize and considered to be more environmentally friendly compared to conventional electrolyte salt because LiBOB does not contain halogen element. This research focused on the synthesis of LiBOB fine powder, which main purpose is improving LiBOB salt solubility in liquid electrolyte solution. This will aid the ion transfer between electrodes which in turn will increase the electrolyte performance. Solid state reaction was employed in this experiment. Synthesis of LiBOB compound was performed by reacting oxalic acid dihydrate, lithium hydroxide monohydrate, and boric acid. The resulting powder was then processed into fine powder using ball milling technique with varying milling time (0, 6, 10, and 13) hour. Microstructure of the sample was then analyzed to obtain information regarding phase formation, functional groups, grain surface morphology, surface area, pore volume, solubility, and ionic conductivity. The analysis shown that LiBOB and LiBOB hydrate phase was formed during the reaction, there was no change in existing phase during milling process, crystallinity index was shifted to lower value but there was no difference in functional groups. Highest value in surface area was found to be 83.11 m²/g, with pore volume of 1.21311e+02 A at 10 hours milling. Smaller powder size resulted in higher solubility, unfortunately the ionic conductivity was found to be decreased.

Abstrak

Sintesis Serbuk Halus LiBOB untuk Meningkatkan Kelarutannya. Senyawa Litium Bis (Oksalato) Borat atau LiBOB mulai banyak diteliti, karena dapat dipergunakan untuk elektrolit pada baterai lithium. Senyawa tersebut mudah disintesis dan dianggap lebih ramah lingkungan dari pada material elektrolit lainnya karena tidak mengandung unsur halogen. Pada penelitian ini dilakukan pembuatan serbuk halus LiBOB. Pembuatan serbuk halus LiBOB bertujuan untuk memudahkan kelarutan LiBOB pada pembuatan elektrolit cair dan memperlancar pergerakan ion dari anoda menuju katoda sehingga meningkatkan kinerja elektrolit. Metode yang digunakan adalah reaksi padat-padat. Sintesis senyawa LiBOB, melalui reaksi antara asam oksalat dihidrat, lithium hidroksida monohidrat dengan asam borat. Serbuk yang dihasilkan kemudian dihaluskan dengan teknik *ball milling* dengan waktu yang bervariasi (0, 6, 10 dan 13) jam. Selanjutnya sampel dianalisis struktur mikro meliputi fasa yang terbentuk, ikatan gugus, morfologi permukaan butir, luas permukaan butiran, volume pori, waktu kelarutan dan konduktivitas listrik. Dari analisa tersebut didapatkan hasil fasa yang terbentuk adalah LiBOB dan LiBOB hidrat, tidak terjadi perubahan fasa selama proses *milling*, indeks kristalinitas perubahan menjadi lebih kecil dan tidak terjadi perubahan ikatan gugus karena pengaruh proses *milling*. Luas permukaan butiran terbesar didapat 83,111 m²/g, dengan volum pori 1,21311e+02 A pada *milling* 10 jam. Semakin halus butiran waktu larut menjadi lebih cepat, tetapi memberikan konduktivitas listrik yang menurun.

Keywords: crystallinity index, fine powder, functional group, morphology, surface area

1. Introduction

In a lithium-ion battery system, electrolyte has an important part as ion media transfer from anode to cathode and vice versa, during charging and discharging process. That being said, electrolyte is a vital component to the battery performance on charging and discharging

capacity, safety, and current density. Electrolyte materials need to have high ionic conductivity, good thermal stability, electrochemical and mechanical properties, inexpensive, safe, and environmentally friendly [1,2,3].

Electrolyte can be in form of solid and liquid electrolyte. Generally, lithium-ion battery is designed to use liquid

electrolyte comprised of lithium salt such as LiPF_6 , LiBF_6 , LiBOB , or LiClO_4 diluted in carbonate alkyl organic solvent. Low interface resistance of LiClO_4 was making it the commonly used electrolyte salt albeit its high oxidation which could be a safety hazard. Its substitute, LiPF_6 , has higher overall performance including better ionic conductivity. One disadvantage of LiPF_6 is the low thermal stability compared to other electrolyte salts [3]. Lithium bis(oxalato) borate or LiBOB has been recently developed as alternative substitute of LiPF_6 for lithium-ion battery. It is considered more environmentally friendly because LiBOB does not contain halogen element which was highly potential to be a pollutant to the environment [4,5,6].

LiBOB is a novel salt found by Lischka et.al in Germany; it possesses good electrochemical stability (~4.5V) and relatively high decomposition temperature, around 320 °C. LiBOB has better thermal stability and higher capacity retention compared to LiPF_6 , but it has lower ionic conductivity [7,8]. LiBOB has all the requirements to be used as electrolyte salt as well as electrolyte additive in lithium-ion battery system [7]. In addition, it has the ability to stabilize graphite anode in a lithium-ion battery with PC (propylene carbonate) solvent. Physical properties of LiBOB i.e molecular weight 193.79 g/mol, density 0.8–1.2 g/cm (20 °C), thermally stable, decomposed at >290 °C temperature (according to TGA analysis), hygroscopic, slowly ionized when in contact with water, solubility level of 17% in propylene carbonate solvent (25 °C), and relatively soluble in mixture of carbonate, carboxyl ester, glymes, ketones, and lactones solvent.

Suitable solvent for liquid electrolyte requires these properties [9]: high dielectric constant to dissolve salt, low viscosity, low freezing point and high boiling point, safe, non-toxic, and inexpensive. Active material used as electrolyte in lithium-ion battery is a lithium salt which role is to carry the charge within the cell during electrochemical process. It requires these properties [10,11]: thermally stable, good solubility and ionization in suitable solvent, chemically stable, high conductivity, low molecular weight, inexpensive, and non-toxic. Beside consideration such as higher ionic conductivity of liquid electrolyte compared to solid electrolyte, liquid electrolyte would be a solution to the problem raised from volume change on the composition of the electrode while charging and discharging. Main concern regarding electrolyte was to expose it to various potential conditions in order to seek after the stable environment. Another disadvantage of liquid electrolyte is the potential leakage, therefore particular design and packaging is required [12].

In this research, LiBOB fine powder has been prepared using milling process. Ball-milling technology employed

collision energy among alumina grinding ball and the milling jar. In obtain fine particle in high quantity and in a relatively short time, an innovation has been made by varying the mill rotation to a planetary movement to adjust the optimal angle of the rotation. The main concept is to increase milling probability by making rotation movement of the grinding ball in a large quantity [13]. Ball mill machine will rotate vial with 12 mm diameter alumina grinding ball. Normal speed rotation is 16 rpm with adjustable milling duration. LiBOB fine powder will be used for the liquid electrolyte in lithium batteries. Fine powder was dissolved in a solvent mixture of carbonate. Based on our previous research, creating a synthesis of liquid electrolyte LiBOB were difficult to dissolve even by using carbonate solvent, so it was necessary to use LiBOB fine powder. Based on lithium battery technology, to increase the capacity of the battery was required nano-sized active material powder. Electrolyte active material with nano size will facilitate the movement of ions between the electrodes.

2. Experimental

Materials. Raw materials used for $\text{LiB}(\text{C}_2\text{O}_4)_2$ synthesis is presented at Table 1.

Equipments. Thermolyne muffle furnace was used for heat treatment in LiBOB compound formation. Ball mill used in this experiment is from MTI XTL specifically SFM-1 Desktop Planetary Ball Miller type. LiBOB powder was characterized using X-Ray Diffractometer (XRD) Rigaku type Smart Lab with $\text{CuK}\alpha$ target, wavelength $\lambda = 1.5406 \text{ \AA}$, *mode continuous-scan* with 2 theta range from 10° to 80° , and step width of 0.01 deg. It was also identified using FT-IR Spectroscopy (Thermo Scientific Nicolet iS-10). This characterization was referring to ASTM E 1252–07 test standard. Electrical conductivity was performed by using conductivity meter Oakton 2700. Microstructure was observed by using scanning electron microscope (SEM) Hitachi SU-350, while particle surface area was observed by using surface area meter Quantachrome Nova 4200e with BET method.

Sample Preparation. LiBOB compound was prepared via reaction path as follows [14]:

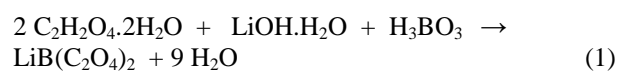


Table 1. Raw Materials as $\text{LiB}(\text{C}_2\text{O}_4)_2$ Precursor

Materials	Chemical Formula	Molecular weight	Purity
Lithium hydroxide	$\text{LiOH} \cdot \text{H}_2\text{O}$	23.96 g/mol	99.8%
Oxalic acid	$\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	12.07 g/mol	99.8%
Boric acid	H_3BO_3	61.83 g/mol	99.8%

Raw materials were weighed based on molar ratio of 2:1:1 then mixed and ground until homogenous, followed by heat treatment at 120 °C temperature for 4 hours and at 240 °C for 7 hours. The resulting powder was $\text{LiB}(\text{C}_2\text{O}_4)_2$ or LiBOB in a form of white powder. Fine powder was prepared by processing LiBOB powder in planetary ball mill with powder and grinding balls ratio of 1:10. Milling duration was varied at 0, 6, 10, and 13 hours.

Crystal Structure Characterization. To observe phase shift or change in crystal structure during milling process in a certain time, characterization was performed using X-Ray Diffractometer. X-Ray diffraction pattern from powder sample was analysed to determine the quality and quantity of the phase. The resulting diffractogram was processed using PDXL software by means of Rietveld refinement method. Beside phase formation data, information regarding crystal structure parameter within one unit cell was also gained from this software, i.e: lattice parameter, mass fraction (for multiphase sample), crystal theoretical density, crystal volume, and space group. Crystallinity index can be calculated empirically with Formula [16].

$$\text{CI} = (\text{I}_{\text{max}} - \text{I}_{\text{min}}) / \text{I}_{\text{max}} \quad (2)$$

Electrical Conductivity. Electrical conductivity measurement was performed to investigate whether milling process performed on LiBOB powder affected the electrical conductivity and solubility of LiBOB in EC/DMC organic solvent.

LiBOB fine powder was dissolved into EC/DMC (1:1 v/v) solvent, mixed using magnetic stirrer for 25 minutes, followed by heating at 50 °C temperature for 10 minutes without mixing. The liquid electrolyte solution was then mixed again on the hot plate at 50 °C for 30 minutes with 500 rpm speed. The solution was cooled down to ambient temperature before performing conductivity measurement. Mixing process and conductivity measurement were done in a glove box with argon atmosphere. During the first step of mixing, the solubility of LiBOB has to be observed manually to investigate the effect of milling time.

3. Result and Discussion

FT-IR spectrum was shown on Fig. 1, which described that the resulting functional groups were referring to fundamental vibration of LiBOB salt [17].

Vibration peaks at wave number 1750 1640, and 1443 cm^{-1} characterised the presence of C=O stretch, COO asymmetric stretch, and COO symmetric stretch, respectively. Fingerprint of LiBOB compound was shown at wave number 1372, 1297, 1070, and 982 cm^{-1} which represented B-O stretch, C-O-B-O-C stretch, O-

B-O symmetric stretch, and O-B-O asymmetric stretch, respectively. Peak at wave number 3513 cm^{-1} showed the presence of hydrate crystal phase in LiBOB product which was characterised with O-H stretch.

Vibration peaks at wave number 1810, 1633, 882, and 723 cm^{-1} were typical fingerprint for LiBOB compound, which showed vibration of C=O oscillation, COO asymmetric stretch, O-B-O asymmetric stretch, and COO bending vibration. Analysis result for various milling time is presented in Table 2.

There were typical functional groups in LiBOB (C_4BLiO_8) compound: C=O vibration at 1781-1818 cm^{-1} , C-O and B-O vibration at 980-1370 cm^{-1} , and OH bond at 3442 cm^{-1} (referring to Journal of Power Sources Vol. 195, Issue 6).

From FT-IR analysis result, it can be seen that there was no change in functional groups as an impact from milling time as the wave number peaks did not show significant shift. Reference [14] also presented similar spectrum of LiBOB sample, which listed O-B-O, C-O-C, and C-O-B-O-C functional groups as present.

XRD analysis result of LiBOB fine powder is presented in Figure 2. Diffraction peaks of lithium bis (oxalato) borate or LiBOB compound appeared in XRD analysis result was referring to ICDD 0917 diffraction pattern, where LiBOB phase possessed orthorhombic structure.

Unwanted phase lithium bis (oxalato) borate hydrate ($\text{LiBC}_4\text{O}_8(\text{H}_2\text{O})$) was found at 2 theta between 19 to 38 degree. This phase was formed because of LiBOB hygroscopic properties resulting in LiBOB binding moisture from air. It was seen from Figure 2 that there were no ominous change in terms of peak position and diffraction pattern. Detailed identification is presented in Table 3.

Crystallinity index calculated from Formula (2) is presented in Figure. 3. It can be seen that crystallinity index was decreased with increasing milling time.

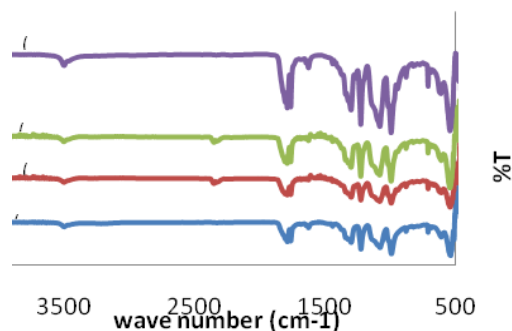
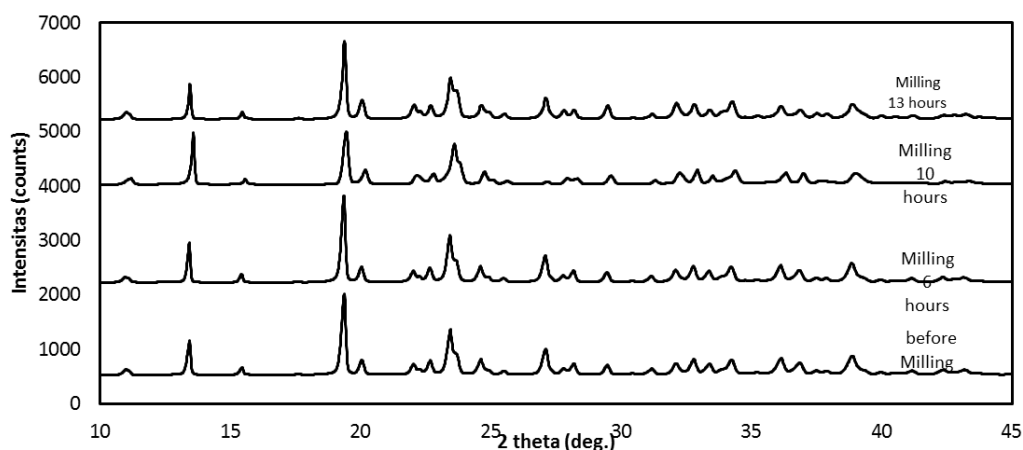


Figure 1. FT-IR Spectroscopy Result of LiBOB Powder with Varied Milling Time (a) 0 Hour, (b) 6 Hour, (c) 10 Hour and (d) 13 Hour

Table 2. Functional Groups Identification of LiBOB Compound with Varied Milling Time

No milling	Wave number (cm ⁻¹)			Functional groups
	6 hours milling	10 hours milling	13 hours milling	
3517.25	3514.17	3517.11	3514.17	O-H
1798.20	1798.23	1798.23	1801.18	C=O oscillate in phase
1765.82	1768.80	1768.80	1768.80	C=O oscillate out of phase
1633.36	-	-	1633.41	COO ⁻ asymmetric stretch
1447.91	-	-	-	COO ⁻ symmetric stretch
1309.57	1306.71	1306.71	1306.71	C-O-B-O-C stretch
1235.98	1227.24	1230.18	1230.18	O-C-C asymmetric stretch and O-B-O bend
1082.91	1085.96	1088.90	1085.96	O-B-O symmetric stretch
997.55	994.72	997.66	997.66	O-B-O symmetric
882.75	879.93	885.82	882.87	O-B-O asymmetric stretch
714.96	712.16	718.05	715.11	COO ⁻ deform
614.88	617.98	617.98	615.03	B-O deform
541.29	544.39	547.34	547.34	BO ₄ deform


Figure 2. Diffraction Pattern of LiBOB fine Powder with Varied Milling Time
Table 3. Identification of LiBOB Sample Diffraction Peak with Varied Milling Time

No milling		6 hours milling		10 hours milling		13 hours milling	
2θ	phase	2θ	phase	2θ	phase	2θ	phase
13.41 ^o	LiBC ₄ O ₈	13.44 ^o	LiBC ₄ O ₈	13.57 ^o	LiBC ₄ O ₈	13.44 ^o	LiBC ₄ O ₈
19.38 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	19.37 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	19.45 ^o	LiBC ₄ O ₈ .H ₂ O	19.40 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O
23.66 ^o	LiBC ₄ O ₈ .H ₂ O	23.46 ^o	LiBC ₄ O ₈	23.79 ^o	LiBC ₄ O ₈ .H ₂ O	23.50 ^o	LiBC ₄ O ₈
27.08 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	27.11 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	27.18 ^o	LiBC ₄ O ₈	27.16 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O
34.22 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	36.13 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	34.36 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	32.13 ^o	LiBC ₄ O ₈ .H ₂ O
38.73 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	38.86 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	38.96 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O	38.85 ^o	LiBC ₄ O ₈ & LiBC ₄ O ₈ .H ₂ O

Linear trend line was obtained from data analysis with equation of $y=0.1715x+98.991$ and $R^2=0.948$. This proved theoretically that fine powder acquired from milling process would give smaller in size. Particle morphology using SEM is presented at Figure 4.

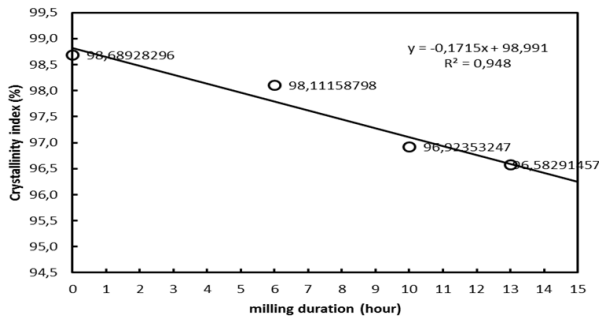


Figure 3. Presentage Crystallinity Index on Various Milling Duration

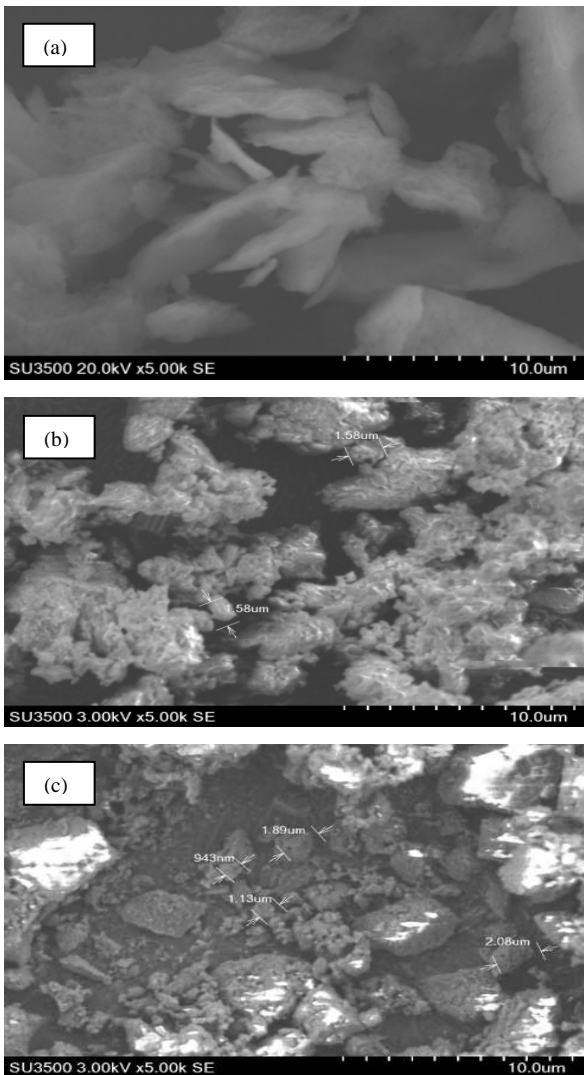


Figure 4. Particle Morphology of LiBOB Powder with (a) No Milling, (b) 10 Hours Milling, and (c) 13 Hours Milling

From SEM images, LiBOB powder with no milling treatment appeared to have flat, thin, and wide form. Milling treatment for 10 hours resulted in more bulky powder, as seen at Figure 4 (b). Further observation showed that smaller, fine powder was acquired in LiBOB powder undergoing milling treatment for 13 hours.

Powder particle surface area and pore size were observed with BET method. The results are presented on Figure 5, Figure 6, and Figure 7.

From particle surface area measurement, significant difference can be seen in LiBOB powder sample before and after milling treatment. Surface area was increasing rapidly until 10 hours milling time, and then slightly

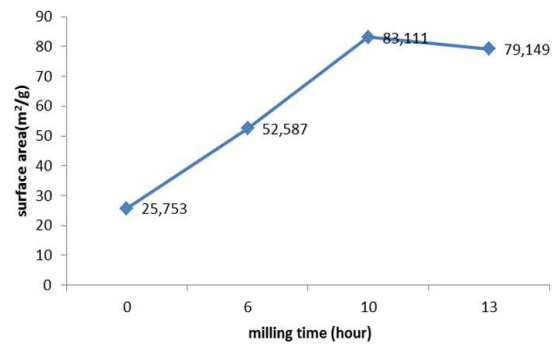


Figure 5. Particle Surface Area on Various Milling Time

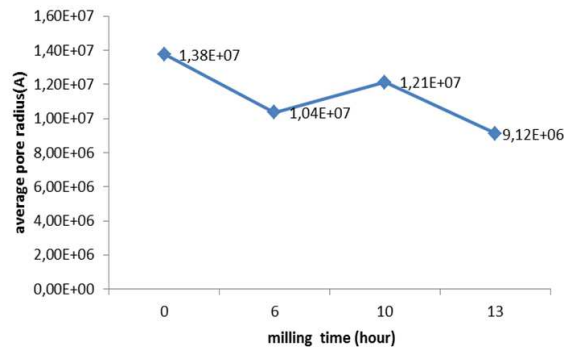


Figure 6. Average Pore Radius on Various Milling Time

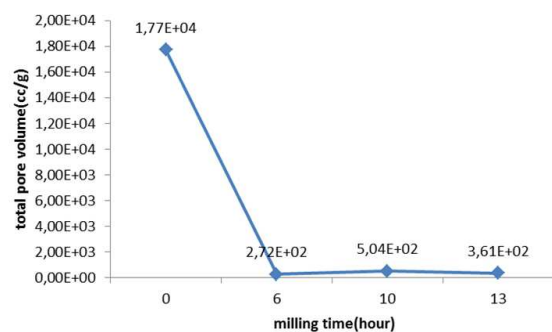


Figure 7. Total Pore Volume on Various Milling Time

decreasing during 13 hours milling time. This is mostly caused by particle agglomeration. On the other hand, pore size and total volume pore showed decreasing trend with increasing milling time.

Solubility of LiBOB compound in EC/DMC carbonate solvent was measured; the results are presented on Figure 8.

In the experiment, LiBOB synthesis produced a powder with large enough surface area to accommodate contact between LiBOB particle and carbonate solvents in liquid electrolyte system. The larger surface areas of a particle, more particles were exposed and the numbers of total collisions are increased, hence the reaction rate was increasing. Therefore, large surface area of LiBOB fine powder were easily soluble in carbonate solvents [18]. LiBOB sample undergoing 13-hour milling time required least time to be fully soluble in the carbonate solvent, because more particle collision has occurred resulting in faster reaction. On the other hand, electrical conductivity of LiBOB liquid electrolyte was decreasing with increasing milling time. This is mainly caused by hygroscopic properties of LiBOB.

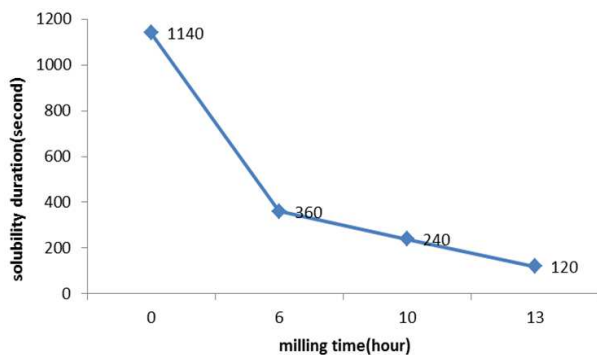


Figure 8. Effect of Milling Duration to Solubility Duration of LiBOB Powder in EC/DMC Carbonate Solvent

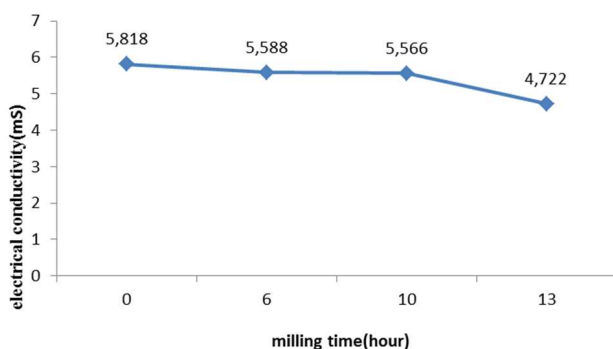


Figure 9. Effect of Milling to Electrical Conductivity of LiBOB Compound

4. Conclusion

There was no phase shifting of LiBOB and LiBOB hydrate phase appeared in LiBOB powder synthesized via solid state method as an effect of mechanical milling, as well as alteration of functional groups. Crystallinity index was found to be decreasing with increasing milling time. On the contrary, higher milling time resulted in faster solubility of LiBOB powder in carbonate solvent. Functional groups was found to be unaffected by mechanical milling. Highest value of particle surface area was $83.11 \text{ m}^2/\text{gr}$ (pore radius of $1.213 \times 10^7 \text{ \AA}$) for sample with 10 hours milling. Hygroscopic property of LiBOB was causing the electrical conductivity to decline with longer milling time, because LiBOB hydrate was formed.

Acknowledgment

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