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Review: Comparison of the LiBH_4 Material Synthesis Method and its Application as Hydrogen Energy Storage

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Abstract

Nano- LiBH_4 is a promising material in technology development, especially as a storage material of the alternative energies that has prospects in the future, i.e. hydrogen. The depleting fossil energy sources requires research and development of renewable energy to fulfil human energy needs on a large scale. This includes the used of methods and materials in storing this energy. This paper aims to review the research results of scientific studies on material sources, methods, and catalysts that can be used to obtain LiBH_4 nanomaterials with a high application rate, especially as a safe storage material for hydrogen energy. This review contains 15 papers from 1945 to 2019 consisting of several LiBH_4 synthesis methods, i.e. ball milling, chemical treatment, electrosynthesis, impregnation, and nano-confinement. The comparison results show that the best method for synthesizing LiBH_4 was ball milling because the process was simple and only requires a short time to obtain the nanoparticles. There are several good material sources for LiBH_4 synthesis, i.e. lithium, boron, Mg-Al waste, metaborate compounds, LiBD_4 , ZnCl_2 , LiH, LiBO_2 , Li_3BO_3 catalyst, commercial LiBH_4 , and mesoporous carbon. Based on the comparison, the best starting material was a mixture of commercial LiBH_4 with mesoporous carbon which produces nano- $\text{LiBH}_4/\text{C}_{\text{mesoporous}}$ with a diameter of 5 nm.

1. Introduction

Hydrides are compounds that form when hydrogen atoms react with more electropositive elements. Some metals and their alloys react with hydrogen to form suitable metal hydrides and these materials can be applied as renewable technologies [1]. One of the most studied hydride categories is metal hydride which is a good hydrogen storage material [2]. Complex hydrides can be ionic or covalent that formed by reaction between BH_4^- , AlH_4^- , or NH_2^- complexes with electropositive metals from groups 1, 2, and 3. Lithium borohydride is a strong reducing agent in organic and inorganic reactions and have molecular weight 21.8 g/mol, melting point 275°C, and decomposed at 320°C [3].

LiBH₄ nanoparticles have potentials in technological development, especially as a hydrogen storage material with a storage capacity of 18.4 wt%. Therefore, LiBH₄ has attracted many scientists to conduct research on its storage capacity and how it can be produced on a large scale in a cost-effective manner [4]. The size of the nanoparticles can reach 1–100 nm. Metal nanoparticles can be made using top-down (physics) and bottom-up (chemistry) approaches [5]. The principle of top-down method is to reduce the particle size to nanoparticles mechanically, while the principle of bottom-up method is to react and develop the molecules into nanoparticles [6]. The approach of making nanomaterials from top-down can be done by using mechanical alloying-powder metallurgy (MA-PM) and mechanical milling-powder metallurgy (MM-PM) techniques such as ball milling and sonication [7].

Based on present research, several synthesis methods of LiBH₄ material, i.e. ball milling, impregnation, nanoconfinement, electrosynthesis, reflux, filtration, and chemical treatment. The starting materials that can be used to synthesize LiBH₄ are lithium, boron, Mg-Al waste, mesoporous carbon, metaborate compounds, LiBD₄, ZnCl₂, LiH, LiBO₂, and Li₃BO₃ catalyst.

This review discusses the comparison of methods and starting materials for the synthesis of the LiBH₄ nanomaterial and its application as an alternative hydrogen storage material. It consists of three parts, i.e. part one—introduction—contains the LiBH₄ material and its applications; the second part contains various material sources, methods, and results of LiBH₄ materials synthesis; and the third part contains summary of the review. The comparison of these methods was presented in Table 1.

Table 1: Materials, methods, results, advantages, and disadvantages of LiBH₄ synthesis.

Materials	Methods	Results	Advantages	Disadvantages	Reference
<ul style="list-style-type: none"> • Pellet LiBH₄ • Matrix Ni 	Impregnation	LiBH ₄ with 500 µm size	Material work at low temperatures	Material size is not nanoscale and it is unstable	Menjo, et al., 2009
<ul style="list-style-type: none"> • Commercial LiBH₄ • Mesoporous Carbon 	Ball Milling	LiBH ₄ with 5 nm diameter	Almost 100% purity with a high specific surface	High operational costs	Zhang, Yao, et al., 2007
<ul style="list-style-type: none"> • LiBH₄ alpha aesar • Aerogel Carbon • CoNiB catalyst 	Nano-confinement	LiBH ₄ that has 6.5 nm pore size and surface area of 151 m ² g ⁻¹	Desorption performance of LiBH ₄ is significantly strengthened.	The mechanism is less clear	Zhao, Yanping, et al., 2013
<ul style="list-style-type: none"> • Metaborate compounds • Mg-Al waste 	Ball Milling	LiBH ₄ with 2 µm size	Low operational costs	LiBH ₄ size does not reach the nano scale	Le, Thi Thu, et al., 2019
<ul style="list-style-type: none"> • LiBH₄ solution • SBA-15 	Nano-confinement	LiBH ₄ with 5 nm pore size	Can work at low temperatures (100°C)	High operating costs	Sun, Tai, et al., 2012
<ul style="list-style-type: none"> • LiBO₂ 	Ball Milling	LiBH ₄ with high purity	High purity	Complicated mechanism	Bilen, Murat, et

• MgH ₂				and requires high cost	al., 2015
• NaBH ₄ • LiBr • THF solvent	– Reflux – Filtration	Clear and solvents-free LiBH ₄	Simple, easy, and economical mechanism	Not good for a large scale.	Brown, Herbert C., et al., 1982
• NaBH ₄ • LiBr • Ethyl ether solvent	– Reflux – Filtration	Clear and solvents-free LiBH ₄	Simple mechanism and high purity	Requires special equipment. The reaction is slow.	Brown, Herbert C., et al., 1982
• LiH • B ₂ H ₆ • Ether solvent	Chemical treatment	LiBH ₄ with purity level about 90%	Simple and inexpensive mechanism	Low purity	Schlesinger, et al., 1951
• KBH ₄ • LiCl • THF solvent	Chemical treatment	LiBH ₄ with purity level of 93.7%	Simple and easy mechanism	The process takes a long time	Raymond Etienne Paul and Nicole Marie Joseph, 1955
• B(OCH ₃) ₃ • H ₂ • LiClO ₄	Electro-synthesis	LiBH ₄ in small quantities	Low cost	The result is less optimal	Omweri, James Mokaya, 2019
• Lithium (Merck 499811) • Boron (Merck 112070)	Ball Milling	LiBH ₄ with good mole ratio	The mole ratio of material is suitable for desired product	Material purity is less than 90%	Çetin Çakanyıldırım and Metin Gürü, 2008.
Lithium Boron	Chemical treatment	Small amount of LiBH ₄	Can used on an industrial or semi-commercial scale in its application	Products are difficult to separate	Filby, Evan E., 1977.
• LiH • LiBH ₄ • ZnCl ₂ • LiBD ₄	Ball milling	Large amount of LiBH ₄	The reaction result of borohydride is close to 100% without reduction in LiD background or LiH contribution	There are still defects that need further investigation	Robin Gremaud, Andreas Borgschulte, Oliver Friedrichs, and Andreas Züttel, 2011.

			between 1850 and 2100 cm ⁻¹		
<ul style="list-style-type: none"> • Lithium chloride • Sodium borohydride 	<ul style="list-style-type: none"> – Reflux – Filtration 	75% LiBH ₄ material conversion results	Low operational costs	Long process	Mattson, Gerald H., 1974
<ul style="list-style-type: none"> • LiH • BF₃ • THF 	<ul style="list-style-type: none"> – Reflux – Filtration 	5.9% LiBH ₄ in solution form.	The reagent easy to handle and uses a "semi-batch" operation whereas the reaction can be controlled in a targeted way and unstable conditions can be avoided.	Low purity levels	Hauk, et al., 2007.

2. Synthesis of LiBH₄

Based on the studies that have been reviewed, there are several kinds of nanoparticle synthesis methods, i.e. impregnation, ball milling, mechanochemistry, chemical treatment, electrosynthesis, and nanoconfinement. LiBH₄ can be synthesized with its metal elements or compounds. These methods and their research results will be discussed further as follows.

2.1. Impregnation

The impregnation method is a preparation method by using a catalyst. There are two kinds of impregnation, i.e. co-impregnation and sequential impregnation. Co-impregnation is known as a method of making catalysts with the aim of forming bimetallic particles by adding two materials together, whereas in sequential impregnation, two materials are added sequentially [8]. This method is used to solve problems that can occur in terms of practical applications. The problem is the formation of fine powder of LiBH₄, LiH, and B which occurs after the reaction and possibly causing losses, e.g. surface poisoning and lowering heat conductivity. The other is overflow of melted LiBH₄ from the sample containers can cause an irregular dehydrogenation reaction [9].

Menjo, et al. (2009) using Ni foam obtained from Sumitomo Electric Industries, Ltd. (porosity 98%, pore size 100-500 μm, thickness and diameter of about 1.5 mm and 10 mm respectively) as a matrix for impregnation. LiBH₄ pellet that has 95% purity was placed on Ni foam in a reaction container. The LiBH₄ pellet melted after the container was heated to 573 K for 120 minutes under 0.5 MPa hydrogen (99.99999% purity) pressure. Thus, the melted LiBH₄ can impregnate the Ni foam. This mechanism can be seen in Figure 1 [9]. The heating temperature was chosen based on the results of research by Nakamori and Orimo in 2004. There were two endothermic reactions for

LiBH_4 corresponding to the structural transition ($T_s = 380 \text{ K}$) and the melting reaction ($T_m = 550 \text{ K}$) [10].

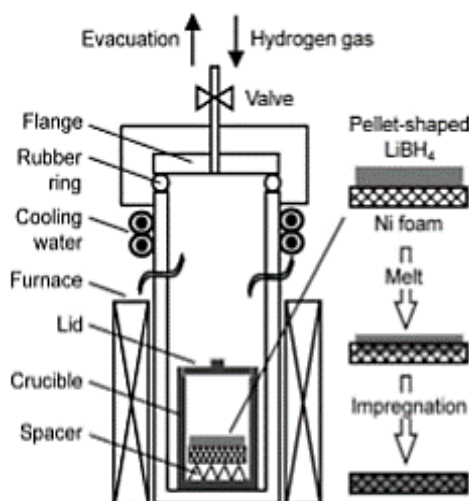
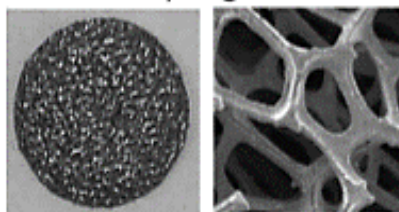
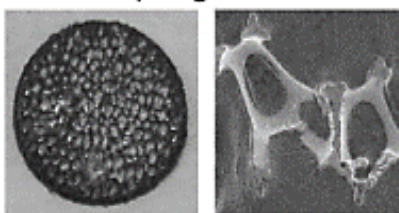


Figure 1: Scheme of impregnation method (the image adapted from Menjo, et al., 2009).

Before impregnation



After impregnation



5 mm

500 μm

Figure 2: Optical microscopy image (left) and scanning electron microscopy (right) from Ni foam, before and after LiBH_4 impregnation (the image adapted from Menjo, et al., 2009).

Figure 2 indicates that LiBH_4 homogeneously impregnated the Ni foam without changing the original bulk morphology of the foam. Based on the results of gas chromatography analysis in Figure 3, the impregnated LiBH_4 has a narrower dehydrogenation temperature range compared to conventional LiBH_4 [9].

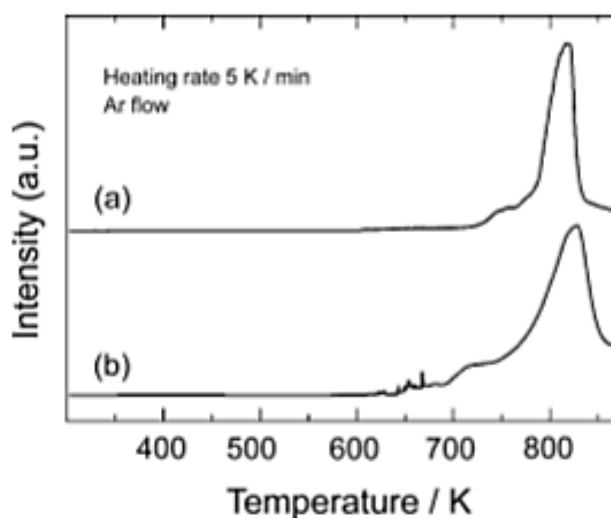


Figure 3: Gas chromatography image corresponding to dehydrogenation reaction of (a) the impregnated LiBH_4 and (b) conventional LiBH_4 (the image adapted from Menjo, et al., 2009).

A small and irregular dehydrogenation reaction occurs at 650 K—shown in Figure 3. This probably coming from overflow of melted LiBH_4 from the sample containers. This was not detected in the impregnated LiBH_4 . Several nickel boride compounds were found to be formed. It depends on heating conditions (dehydrogenation). This formation probably dominates the microstructure and dehydrogenation properties of impregnated LiBH_4 [9].

Based on the research of Menjo, et al. (2009), we conclude that LiBH_4 produced by this impregnation method has advantages, i.e. the bulk morphology remains same after being heated at various temperatures. This method also works at a temperature that is not too high. However, the size of LiBH_4 does not reach the nanoscale and is less stable due to the possibility of nickel boride formation.

2.2. Ball Milling

Ball milling is a mechanical technique that is widely used to grind powder into fine particles and mixed materials [11]. Ball mill is a machine that can convert glass particles into granular particles. This machine contains grinding particles that can be perfectly made from glass. With this machine, we can capture grain size particles perfectly [12].

There are various types of ball mills based on their function. The ball mill has small balls which are used as grinders. The small balls can be made of steel, stainless steel, ceramic, or rubber. It depends on the energy released from the collision and friction between the ball (grinding or grinding medium) and powder [13]. The ball mill also consists of a hollow cylindrical shell that rotates around its axis [12].

Ball milling has several advantages, i.e. cost effectiveness, reliability, and ease of operation. The results of this method can also be reproduced because the energy and speed can be controlled. This method can also be applied in wet and dry conditions to various materials (e.g. cellulose, chemicals, fibers, polymers, hydroxyapatite, metal oxides, pigments, catalysts) [13].

2.2.1. Commercial LiBH_4 and Mesoporous Carbon

Zhang, et al. (2007) synthesized LiBH_4 with mesoporous carbon using a ball mill with a mixture ratio of 1: 1. The mixture was ground upon a QM-ISP planetary ball miller for 5 hours at 450 rpm. The ball mill used was made of stainless steel. In each milling pot (100 ml), the weight ratio of ball-to-powder was 40:1 and the protection atmosphere was 0.3 MPa H_2 [14].

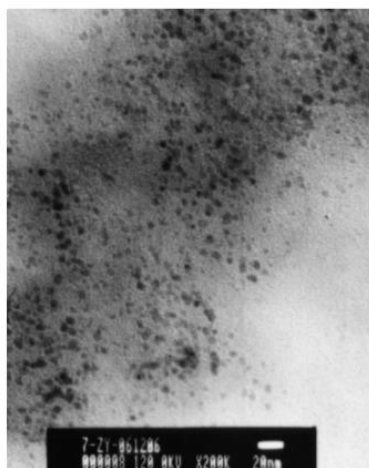


Figure 4: TEM micrograph for nano- $\text{LiBH}_4/\text{C}_{\text{mesoporous}}$ (the image adapted from Zhang, et al., 2007).

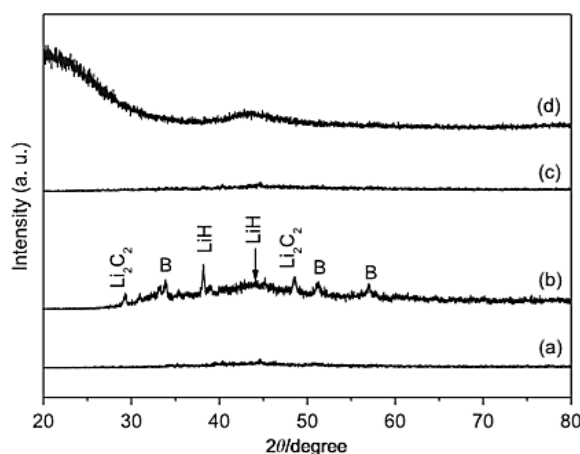


Figure 5: XRD patterns for (a) nano- $\text{LiBH}_4/\text{C}_{\text{mesoporous}}$ before dehydrogenation, (b) nano- $\text{LiBH}_4/\text{C}_{\text{mesoporous}}$ after dehydrogenation at 350°C, (c) nano- $\text{LiBH}_4/\text{C}_{\text{mesoporous}}$ after rehydrogenation at 350°C under 3 MPa for 100 hours and (d) pure CMK-3 (the image adapted from Zhang, et al., 2007).

LiBH_4 nanoparticles were supported by the mesoporous carbon with unarranged structure, CMK-3 [14]. The material denoted as nano- $\text{LiBH}_4/\text{C}_{\text{mesoporous}}$. Commercial LiBH_4 95% was used without further purification. Mesoporous carbon CMK-3 was synthesized using silica SBA-15 as template and sucrose as carbon source [15]. TEM and XRD were used for sample observation. The results of these observations can be seen in Figures 4 and 5 [14].

LiBH_4 particles that have been crushed have a nanometer size with a diameter of about 5 nm. The latent heat of dehydrogenation obtained from the calculation is 40 kJ/mol H_2 . This value is lower than bulk LiBH_4 which has a latent heat of dehydrogenation of 67 kJ/mol H_2 . Based on these results, the dehydrogenation process is thermodynamically beneficial. The melting peak of LiBH_4 shifted to the left and weakened. This proves the existence of thermal stability [14].

Dehydrogenation quantification showed nano-LiBH₄/C_{mesoporous} undergoes H₂ desorption more than 7 wt% under 600°C. This value is the same as 14 wt% H₂ desorption from LiBH₄ and slightly higher than the bulk LiBH₄ sample which undergoes 13 wt% H₂ desorption under 600°C. Rehydrogenation of samples can be performed well under 3 MPa [14].

The XRD patterns reflected each product phase before and after nano-LiBH₄/C_{mesoporous} de-/hydrogenation process. Based on Figure 5 (a), carbides or other phases could not be found in original nano-LiBH₄/C_{mesoporous}. The LiBH₄ peaks can hardly be identified from the pattern because of the nanometer particles. Mesoporous carbon also cannot be clarified because it is amorphous as shown in Figure 5 (d). After dehydrogenation at 350°C, the product phase consists of LiH, Li₂C₂ and boron in Figure 5 (b) [14].

Mesoporous carbon function as a reactive agent for the decomposition of LiBH₄ or LiH. Both mechanisms have a synergistic effect on the dehydrogenation of nano-LiBH₄. Mesoporous carbon CMK-3 plays a dual role in this, i.e. as a support and reactive agent. Moreover, their purities nearly 100% and its specific surface significantly higher than some other types of carbon materials (e.g. carbon nanotubes, nanofibers, etc.), have the potential for further applications. This type of carbon material can not only absorb hydrogen, but also adsorb hydrogen at 350°C [14].

Based on the research of Zhang, et al. (2007), we concluded that the synthesized nano-LiBH₄/C_{mesoporous} has advantages, i.e. its size reaches the nanoscale with a diameter of 5 nm and its dehydrogenation latent heat is lower than bulk LiBH₄. This is thermodynamically advantageous. The product is also thermally stable. However, this nano-LiBH₄/C_{mesoporous} is difficult to identify by XRD.

2.2.2. Metaborate compounds and Mg-Al waste

Li, et al. (2019) synthesized LiBH₄ (the term in this study was LBOM) using cheap materials, such as LiBO₂ and Mg-Al waste. 3.121 g of Mg – Al waste that had been previously prepared were milled with 2.43 g of LiBO₂ for 1-36 hours with milling temperature of 25 - 40°C. The milling tool is the Simoloyer CM08. This method can be quite effective. The results of the analysis proved that LiBH₄ was successfully synthesized under 70 bar H₂ at room temperature using the ball milling method. The conversion efficiency of LiBH₄ obtained was more than 99.5%. Calculation from the composition of LiBO₂ + 2Mg with the total amount of Mg-Al based on waste: 2.5 mol and carried out under 70 bar H₂ [16]. This shows that the Gibbs free energy was very negative as was done in [17].

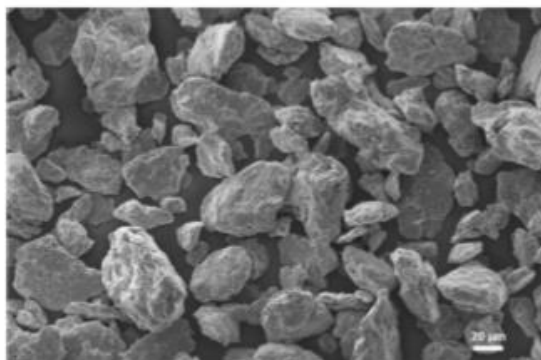
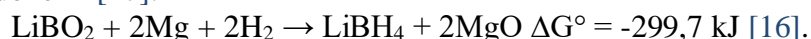


Figure 6: SEM image for grinded Mg-Al based on waste (the image adapted from Li, et al., 2019).

Samples were characterized using SEM and XRD techniques. The results of these characterizations were shown in Figures 6, 7, and 8. Based on the LBOM_1 diffraction pattern, the diffraction peaks of Mg and LiBO_2 were still visible. In the characterized LBOM_12, LBOM_24, and LBOM_36 patterns, there were only MgO diffraction peaks. Thus, this causes the crystalline formation of LiBH_4 cannot be observed by XRD [16].

Based on research of Li, et al. (2019), we conclude that this method was quite effective and easy to do. The result of Gibbs free energy was very negative, means the reaction was spontaneous, that high temperatures are not required. However, the product size does not reach the nanoscale.

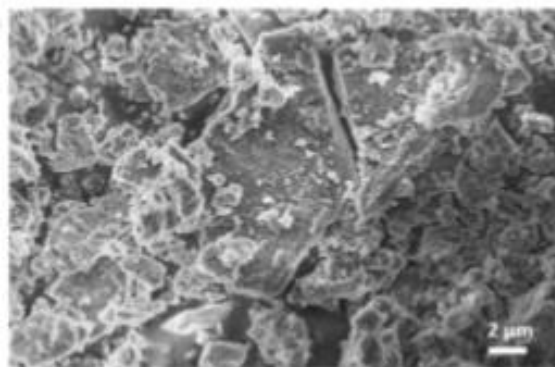


Figure 7: SEM image of LBOM_36 sample (the image adapted from Li, et al., 2019).

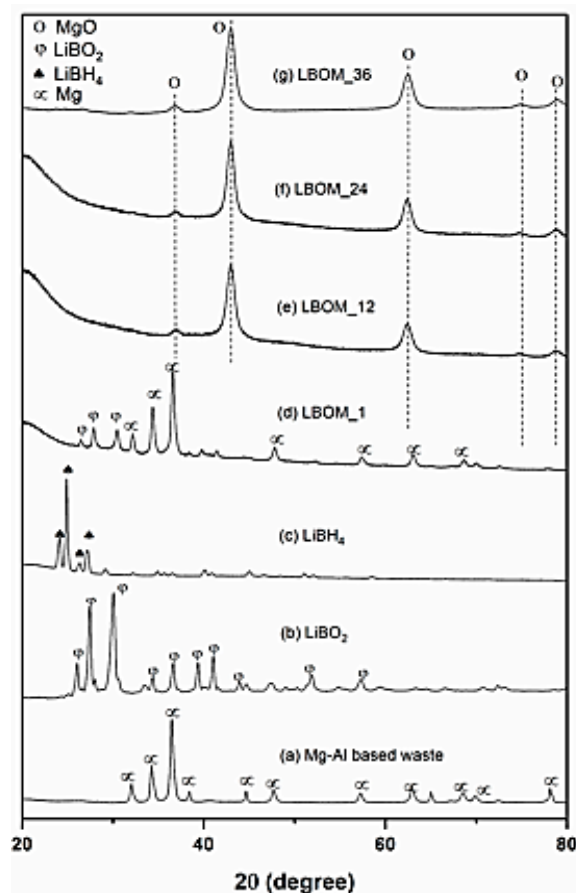


Figure 8: XRD patterns of (a) Mg-based alloy; (b) LiBO_2 ; (c) LiBH_4 ; (d) LBOM_1; (e) LBOM_12; (f) LBOM_24, and (g) LBOM_36 (the image adapted from Li, et al., 2019).

2.2.3. LiBO₂, MgH₂, and CoI₂ Catalyst

Bilen, et al. (2015) used LiBO₂ and MgH₂ materials in the synthesis of LiBH₄ with MgH₂/LiBO₂ mole ratios of 0.65, 1, and 1.3. The duration of ball milling was 300, 600, 800, and 1000 minutes. The tool used was the same as the previously research, i.e. the Spex 8000 M [18].

LiBH₄ was synthesized using LiBO₂, MgH₂, and CoI₂ catalyst through the ball milling. The synthesized LiBH₄ needs to be purified to reach a purity level of 90% and is crystalline. Product yield increases with working time. The optimum reaction time of ball milling was 1000 minutes. The best MgH₂/LiBO₂ reactant ratio to use was 1:0 [18].

CoI₂ supported on AC and added with stearic acid to decompose LiBH₄. 40 wt% CoI₂ on AC can reach 148 mL/min g-cat at 20°C, 1275.06 mL/min g-cat at 70°C. The dehydrogenation activation energy was 33.12 kJ/mol and this was zero order kinetics [18].

The result of LiBH₄ decomposition rate can be used by the fuel cell system in the absence of a high level of consumption. The hydrogen generation rate and the efficiency of its dehydrogenation process need to be further improved through studies on the synthesis of nano-sized catalysts and additives that can increase the activity and lifetime of catalysts [18].

Samples were characterized using XRD and carried out at different working times. The XRD software performs calculations with the Scherrer equation. The results were shown in Figure 9 and proved that the product was crystalline and the particles were nano-sized [18].

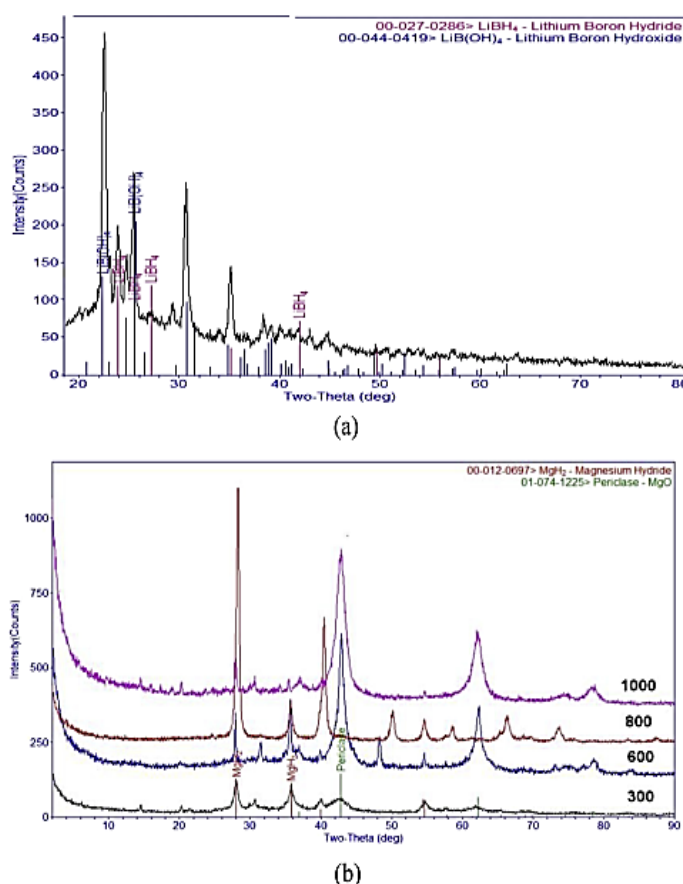


Figure 9: XRD diffraction of (a) the synthesized LiBH₄ from solution and (b) cake filtration (MgH₂/LiBO₂ ratio was 1, 1000 minutes) (the image adapted from Bilen, et al., 2015).

Based on the research of Bilen, et al. (2015), we concluded that the synthesized LiBH_4 had a high level of purity and reached the nanoscale. However, the size of the nanoparticles was not exactly known.

2.2.4. Lithium (Merck 499811) and Boron (Merck 112070)

Çakanyıldırım and Gürü (2008) synthesized LiBH_4 using lithium and boron metal materials. The metal elements were put into the reactor and mixed in a Spex attritor type (CertiPrep 8000M) for 200 minutes. The time spent in their study was shorter than that of Zhang, et al. This is probably due to the type of material, the amount of material, and the volume of tools they used. They synthesized LiBH_4 starting from the elements using an attritor (ball mill) through a solid phase reaction and pressurized hydrogen. This is a new method. LiB has been proven to be used as a hydrogen storage material and this development can be used to guide the application of technology for supplying hydrogen to fuel cells [19].

The absorption of hydrogen on LiB is a chemical process. If the appropriate mole ratio ($\text{B/Li} = 0.214$) was used, the technique was successful for producing LiBH_4 . This conclusion was supported by experiment. The strong peak vibration ($2200\text{--}2400\text{ cm}^{-1}$) corresponding to the B–H bond is shown in the FT-IR analysis in Figure 10. Furthermore, the catalytic desorption process led to the release of 1972.94 mL H_2 from 1 g of impure LiBH_4 . This yield was equivalent to 90% of the hydrogen that commercial LiBH_4 has. Since the purity of the synthesized LiBH_4 was very less than 90%, hydrogen was generated from the sample and water that added [19].

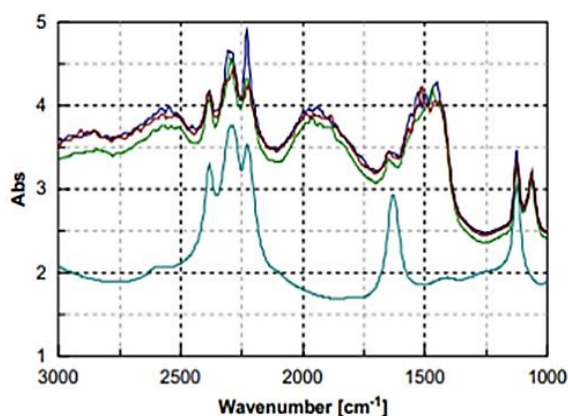


Figure 10: FT-IR image of B/Li hydration (0,214 mol) that has done after ball milling with three types of vessel (the image adapted from Çakanyıldırım dan Gürü, 2008).

2.2.5. LiH, LiBH_4 , ZnCl_2 , and LiBD_4

Gremaud, et al. (2011) mixed LiBH_4 and ZnCl_2 with a ball mill Spex 8000 M for 90 minutes so the metathesis reaction could occur. The tools used were the same as Çakanyıldırım and Gürü [19], but the time used was shorter. Several factors influence these differences, i.e. the type of material used and the results to be achieved [20].

In this synthesis, isotopes label lithium hydride and diborane in reaction (2) by: $\text{LiH} + \frac{1}{2} \text{B}_2\text{D}_6$ to understand the mechanisms that drive the formation of alkaline borohydrides. The stretching of BH and BD in Raman spectra for isotope configurations with reference spectra of LiBD_4 and LiBHD_3 is shown in Figure 11 [20].

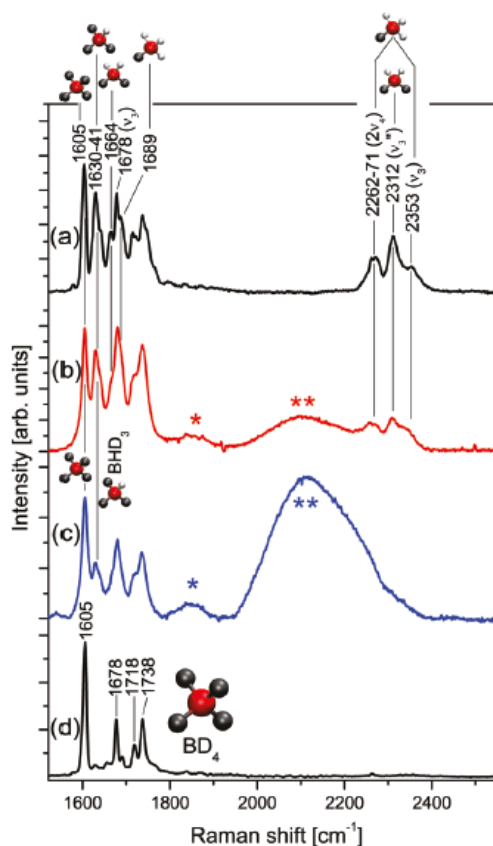


Figure 11: Comparison between LiBH_4/D_2 dan $\text{LiH}/\text{B}_2\text{D}_6$ solid-gas reaction. (a) Raman spectrum at 190°C of LiBHD_3 obtained by exposure of LiBH_4 to 20 bar D_2 gas at 265°C for 24 h. Unless otherwise specified, the labels indicate the ν_1 stretching mode frequencies of the various $\text{BH}_{4-n}\text{D}_n$ isotopomers. Red, gray, and white balls represent boron, deuterium, and hydrogen atoms, respectively. (b) Room-temperature Raman spectrum of LiH exposed to a 1 bar $\text{B}_2\text{D}_6/\text{D}_2$ 1:1 gas mixture for 14 h at 140°C ; (c) same as (b) but for a gas exposure at 100°C . Spectra are corrected for the broad LiH background spectrum. Stars indicate remaining second order LiH Raman peaks. (d) Raman spectrum of LiBD_4 at -190°C . Spectra are shifted vertically for clarity (the image adapted from Gremaud, et al., 2011).

The Raman measurement prioritizes the initial and final reaction states for the formation of LiBH_4 from the labeled diborane and the appropriate reaction pathways. However, side reactions are possible. It was still possible to measure the start and end states. The presence of several isotopomers (not just one) was an indication of an exchange reaction. In an extreme case, there might be the three reaction paths as follows:

1. $\text{LiD} + \text{B}_2\text{H}_6 \rightarrow \text{LiD} + \text{BH}_4^-\text{BH}_2^+ \rightarrow \text{LiBH}_4 + \text{BH}_2\text{D}$
2. $\text{LiD} + \text{B}_2\text{H}_6 \rightarrow \text{LiD} + \text{BH}_3 + \text{BH}_3 \rightarrow \text{LiBH}_3\text{D} + \text{BH}_3$
3. $\text{LiD} + \text{B}_2\text{H}_6 \rightarrow \text{LiD} + \text{BH}_3 + \text{BH}_2\text{D} \rightarrow \text{LiBH}_4 + \text{BH}_2\text{D}$

Considering only the initial and final states, reaction (1) cannot be distinguished from reaction (3). Four different peaks appeared in the stretch region of BD , i.e. at 1712, 1677, 1641, and 1612 cm^{-1} . The four peaks can be seen in Figure 11 [20].

2.3. Nanoconfinement

The nanoconfinement effects have been studied to understand and modify the thermodynamic and kinetic properties of energy storage materials and improve their cyclic behavior. Its direction depends on the degree of destabilization of each material on each side of the equation. If the educt is more unstable than the product, the system is generally considered to be "unstable" [21].

Nanoconfinement polymers take nanometer-scale dimensions and yield distinctive thermodynamic and kinetic properties due to size and interface effects [22].

Nanoconfinement can limit the mobility of the desorption product thereby creating a close contact between the hydride and the porous scaffold. Therefore, reversibility and stability can be significantly improved. Several cases have shown that nanoconfinement has effectively changed the decomposition properties of materials for hydrogen storage [23]. The most important is the mass spectroscopic analysis showing that nanoconfinement can suppress or eliminate the release of diborane and imply a reaction pathway leading to higher borane species with controlled breakdown of borohydride. This is a breakthrough in the reversibility of borohydride for hydrogen storage due to the formation of very stable closoborane species [24].

2.3.1. LiBH₄ Solution and SBA-15

Sun, et al. (2012) used this method to produce 33 wt% LiBH₄. This can be obtained by mixing 4.5 mL of LiBH₄ in THF with 0.4 g of SBA-15 gradually until all the support material was completely moistened. Then, the mixture was stored in a glove box for 24 hours before drying in a freeze dryer (CHRIST Alpha 2-4 LD Plus) for another 24 hours. Freeze dryer in clean state and under high vacuum environment. This ensures that the LiBH₄ nanoparticles and SBA-15 do not react with each other prior to measurement [25].

The SBA-15 used is a short rod with a one-dimensional canal with a diameter of about 9 nm and the mesoporous arrangement is a regular hexagonal shape. In Figure 12, the LBH/SBA-15 mesoporous structure remains unchanged after the loading process, but the pore diameter decreases by about 5 nm. This proved that LiBH₄ was successfully loaded into the pores of SBA-15. This was due to the strong capillary effect. Based on the XRD results from LBH/SBA-15, no sharp peaks of LiBH₄ can be observed. The wide peaks in the 15–25° range indicate that the LiBH₄ contained was in an amorphous or fine crystallite state. Meanwhile, two characteristic bands at 2273 and 2304 cm⁻¹ in the FTIR spectra for LBH/SBA-15 proved the presence of the BH₄⁻ group (Figure 13) [25].

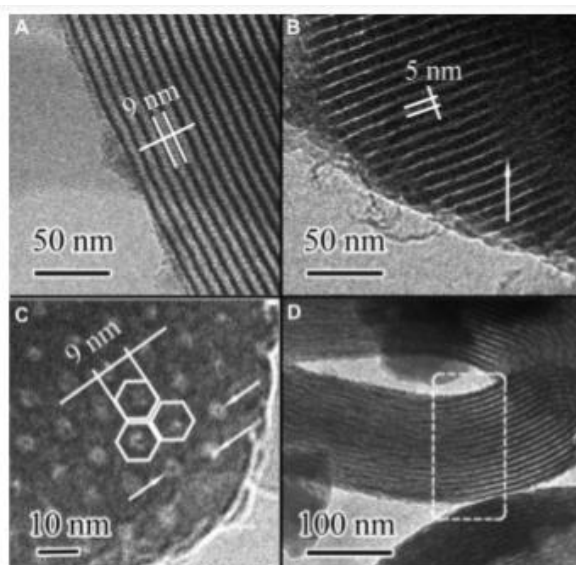


Fig 12: TEM image of (a) SBA-15 and (b) LBH/SBA-15 seems normal to pores axis; (c) LBH/SBA-15 along pores axis; (d) dehydrogenated LBH/SBA-15 (the image adapted from Sun, et al., 2012).

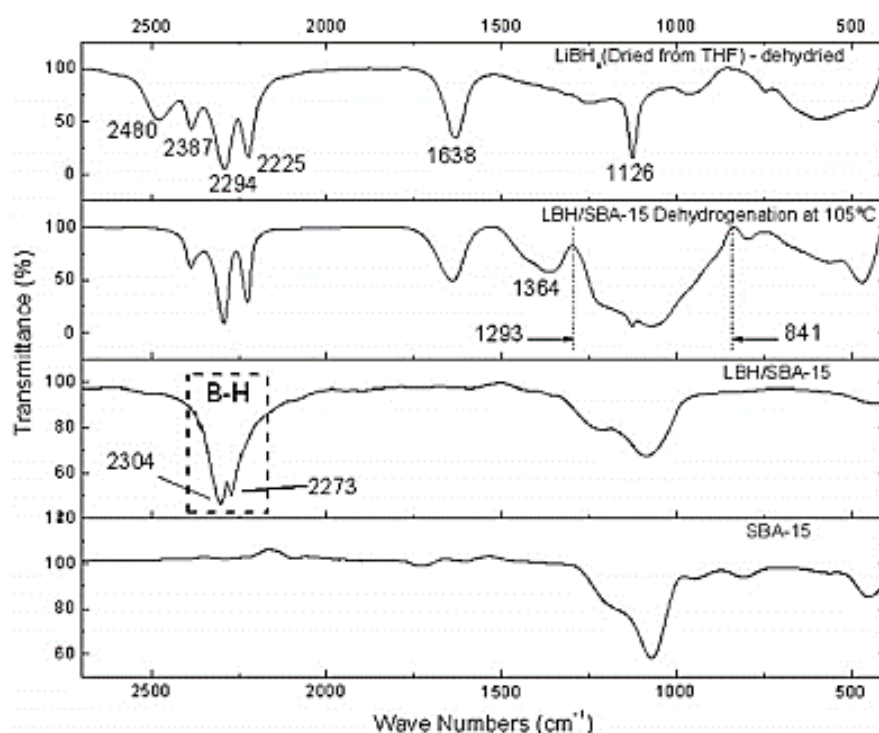


Figure 13: FTIR spectra of SBA-15, LBH/SBA-15 sample as prepared and after dehydrided at 105°C. SBA-15 is given as a reference. Peaks at 2273 and 2304 cm^{-1} correspond to different stretching modes of B—H bonds, which confirm the presence of BH_4^- group in as-prepared sample (the image adapted from Sun, et al., 2012).

The size and destabilization effects of LiBH_4 undergo nanoconfinement and the reaction between LiBH_4 and SiO_2 in the LBH/SBA-15 system caused the peak of LiBH_4 main hydrogen release was drastically decrease under 100°C. Hydrogen was rapidly released from LiBH_4 in an amount of 8.5 wt% in 10 minutes reached at 105°C [25].

2.3.2. LiBH_4 Alfa Aesar, Aerogel Carbon, and CoNiB Catalyst

Zhao, et al. (2014) used this method to synthesize LiBH_4 by dissolving 176 mg of LiBH_4 in 3.5 mL anhydrous THF. The solution was added to the nanocomposites CA@CoNiB in an evacuated Schlenk flask and refilled with Ar which flowed into the bubbler. The mixture was stirred for 3 hours, then dried at 80°C for 72 hours to remove the THF solvent and produce a dark brown powder [23].

The LiBH_4 preparation was confined in aerogel carbon with a CoNiB load via chemical impregnation method. The $\text{LiBH}_4\text{-CA-CoNiB}$ samples obtained showed superior dehydrogenation properties. The desorption temperature and desorption kinetics quickly become lower due to the synergistic effect between the catalyst and the confinement. The initial and peak desorption temperatures of $\text{LiBH}_4\text{-CA-CoNiB}$ were 192 and 320°C, respectively. The temperature was reduced by about 100°C when compared to LiBH_4 bulk. Meanwhile, isothermal dehydrogenation curves showed that the $\text{LiBH}_4\text{-CA-CoNiB}$ samples produce desorption kinetics better than pure LiBH_4 , $\text{LiBH}_4\text{-CoNiB}$, and $\text{LiBH}_4\text{-CA}$. Thus, the mixed catalyst in porous carbon has the potential to improve the decomposition properties of LiBH_4 . However, the mechanism is not clear, so it needs to be investigated further [23].

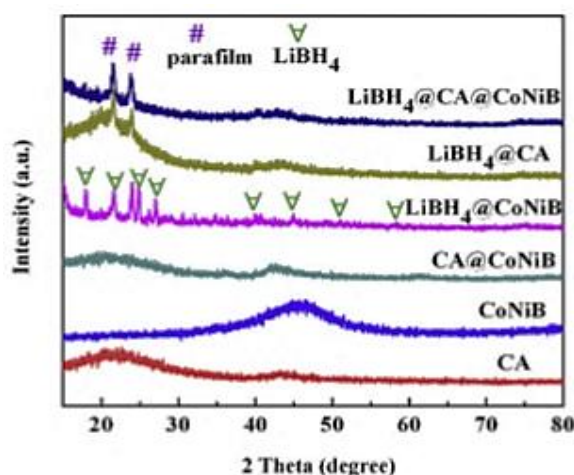


Fig 14: XRD patterns of CA, CoNiB, CA-CoNiB, LiBH₄-CoNiB, LiBH₄-CA, LiBH₄-CA-CoNiB (the image adapted from Zhao, et al., 2014).

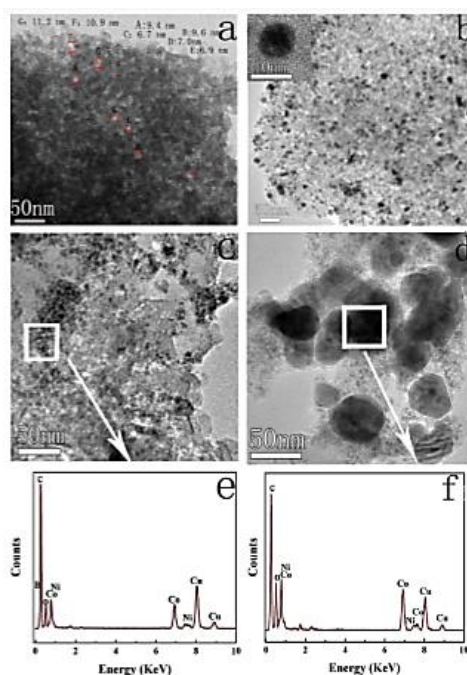


Figure 15: TEM image of (a) CA, (b) CoNiB, (c) LiBH₄-CA-CoNiB and (d) dehydrogenated LiBH₄-CA-CoNiB at 400°C. (e,f) EDX LiBH₄-CA-CoNiB before and after desorption (the image adapted from Zhao, et al., 2014).

LiBH₄ was characterized using XRD (Figure 14) but cannot be described by TEM/EDX (Figure 15) because of its weak scattering of electrons through the light elements Li and B. Nanoconfinement can produce shorter diffusion pathways, lower energy limits, and very close between the LiBH₄ and CoNiB nanoparticles. Nanomaterials usually have a stronger catalytic effect than bulk materials. Therefore, the confined CoNiB nanoparticles in small pores can provide more active sites for their catalytic effect on the decomposition of LiBH₄. Electrons can be transferred from atom B to the empty d orbital of Co/Ni so that the Co/Ni metal was rich in electrons. During the dehydrogenation process, the interaction between Li atom and aerogel carbon was an ionic interaction. The BH₄ unit was absorbed chemically on the active site of Co/Ni. Then, the active side gives negative charge—that is electron—to the BH₄ ion, which stimulates hydrogen emission [23].

2.4. Reflux and Filtration

Solvent recycled reflux extraction is an extraction process in which a solution is simultaneously extracted and concentrated [26,27]. Gong et al. (2014) explained that the extract in the extraction tank is pumped out and concentrated in the concentration tank during the extraction process. Meanwhile, the evaporated solvent is condensed and pumped back into the extraction tank. As the solvent is renewed during the extraction, the driving force of mass transfer is greater and cause the extraction times shorter. Reuse of solvents in extraction also decreases the amount of required solvent [27].

Daniel et al. (2010) explained that liquid filtration involves separating soluble and insoluble species from a liquid stream using a solid membrane. Separation is accomplished by bringing the solution, sol, or slurry into contact with the filter media (membrane) and forcing the flow of liquid through the membrane and applying a pressure gradient across the membrane. As the liquid passes through or through the membrane, the filter holds (or filters) a fraction of the solid and dissolved species [28].

In their book, Daniel et al. (2010) stated that filtration operations can use a dead-end or crossflow filtration configuration. The two configurations differ in the flow direction of the slurry or bulk solution relatively to the filter surface. In dead-end filtration, the slurry flow normally flows to the filter membrane. The solids retained by the membrane remain on the membrane surface, forming a filter that grows proportionately to the filtered volume. The build-up of solids increases the resistance to absorb flow over time [28].

2.4.1. Lithium Chloride and Sodium Borohydride

Mattson (1974) used lithium chloride and sodium borohydride in the synthesis of LiBH_4 . About 4 g (~ 0.015 g mol.) of sodium borohydride was cleaved and placed in a reaction flask. About 280 mL of 1 molar lithium aluminum hydride (~ 10.62 g, i.e. 0.28 g mol. LiAlH_4) in diethyl ether solution were added at room temperature and atmospheric pressure. The mixture was stirred. Meanwhile, about 70 mL of AlCl_3 (concentration of 1 mole in diethyl ether solution, i.e. 0.07 g mol. of AlCl_3) was added from the dropping funnel during period of 20 to 30 minutes. This gives a mixed reaction in which the $\text{AlCl}_3/\text{LiAlH}_4$ ratio was about 75% of the required for the stoichiometric reaction between LiAlH_4 and AlCl_3 to give AlH_3 and LiCl . After addition of aluminum chloride, solids (especially lithium chloride, sodium chloride and excess sodium borohydride) were filtered [29].

The residual solid waste was analyzed by X-ray diffraction and its chemical elements showed that about 75% of sodium borohydride was converted to lithium borohydride. The resulting lithium aluminum hydride-aluminum hydride-lithium borohydride solution has a g mole proportion of lithium aluminum hydride/lithium borohydride about 1/1.28. Furthermore, both were used directly in the production of white aluminum—that was aluminum hexagonal hydride with a relatively large particle size. Similar in situ production of lithium borohydride in high yield by the same procedure was realized using a molar proportion of lithium aluminum hydride/sodium borohydride ranging from about 1/1 to about 1/0.25 [29].

2.4.2. Synthesis of LiBH_4 in THF, $\text{LiH}:\text{BF}_3$ Ratio 4.73:1

Hauk, et al. (2007) used THF as solvent in this method. The LiH:BF₃ ratio used was 4.73:1. 42.4 g (5.34 mol.) of ground lithium hydride in 300 g of THF placed in a 0.5 L double-walled reactor drained with argon and equipped with a reflux condenser, thermocouple, conductivity measuring probe, drip funnel and gas washer (filled with 145 g acetone). After the addition of 1.1 g solid lithium borohydride, the internal temperature was raised to 53°C and measurement of the BF₃.THF complex (total 158.1 g: 1.13 mol.) was initiated [30].

The reaction started without delay. This can be seen by a sudden increase in internal temperature from 53 to 59°C within 5 minutes and an increase in conductivity from 0.03 to 0.10 mS/cm. To be better, heat dissipation with jacket temperature was measured up to 45 °C. BF₃.THF was added for 90 minutes. Boron (<0.005 mmol/g) was not detected in gas washer filled with THF [30].

2.4.3. LiBr and NaBH₄ with THF and Ether Solvents

Brown, et al. (1982) conducted two tests using reflux and filtration methods, i.e. isopropylamine and ether. The two procedures were the same, but the solvents used were different. The reaction was carried out under a nitrogen atmosphere at the desired reaction temperature (0°C, 25°C, and reflux temperature). In a special procedure, lithium halide (0.8–1.0 M) was treated with NaBH₄ (0.8–1.0 M) dissolved (IPA) or suspended in a suitable solvent [31].

The conversion of NaBH₄ to LiBH₄ occurs through a metathesis reaction with lithium halide in selected aprotic solvents. Strong magnetic stirring has a large effect on the conversion process. The inclusion of glass granules into the reaction mixture mechanically stirred increases the reaction rate. It was facilitating the synthesis of LiBH₄ in a simple ether solvent. The clear solution of LiBH₄ can easily be separated from the precipitated sodium halide. The order of ease of solvent separation was EE > IPA > THF > 1,3-D = MG. The metathesis reaction in ether provides a practical and good method for preparing LiBH₄ solvent-free. As an alternative, the addition reaction between BMS and LiH in ether was an easy step to synthesize LiBH₄. This study establishes a simple economic path for the preparation of LiBH₄. This development should increase the usefulness of reagents for selective reduction in organic synthesis [31].

2.5. Chemical Treatment

Chemical treatment is the most common technique for proper functioning of polymer surfaces and uses chemical species (gases or solutions) which react with existing polymer functional groups. Chemical reactions can be carried out on structures such as benzene rings, hydroxyl groups, double bonds, halogens, and ester groups in polymer molecules—which are susceptible to electrophilic or nucleophilic attack [32,33].

2.5.1. LiH, B₂H₆, and Ether Solvents

Schlesinger, et al. (1945) used LiH and B₂H₆ materials with the help of ether solvents. Lithium hydride—have a particle size of approximately 200 mesh—is added into the reactor through the tube neck. 50 cc anhydrous diethyl ether was added through the reactor neck. 1 L of diborane gas (under standard conditions) was condensed in a gas ball using liquid nitrogen and a tightly closed bottom ball connected to the reactor. Then, the gas ball containing diborane was opened to the reactor. Diborane was forced into the reactor by heating the gas ball. As the temperature of the gas ball could rise to near room temperature, the reactor temperature was lowered substantially using

liquid nitrogen. Such cooling accelerates the flow of diborane from the gas ball to the reactor. After the inclusion of the diborane was completed, the reactor was closed, and the cooling of the reactor was stopped [34].

Based on the research of Schlesinger, et al. (1945), there were several key points as follows:

- The process of forming LiBH_4 was carried out by reacting $2\text{LiH} + \text{B}_2\text{H}_6$. This reaction was carried out by changing the temperature from 0 to 50°C ;
- The used of lithium hydride in this reaction was recommended in the form of a fine powder with a particle size of 100 to 200 mesh;
- The reaction between $2\text{LiH} + \text{B}_2\text{H}_6$ formed 2LiBH_4 assisted by ether;
- The ether solution acts as a solvent for lithium borohydride and can increase the reactivity of boron;
- During reactions, lithium borohydride solutions often crystallize. The way to anticipate this was to warm the ether solution;
- The formation of 2LiBH_4 from the reaction between $2\text{LiH} + \text{B}_2\text{H}_6$ was assisted by the presence of diethyl ether, dimethyl ether, and dipropyl ether;
- The method of forming 2LiBH_4 from the reaction between $2\text{LiH} + \text{B}_2\text{H}_6$ does not contact with free air;
- In the presence of ether, the reaction was faster and more efficient [34].

2.5.2. KBH_4 , LiCl , and THF Solvent

Paul and Joseph (1955) used KBH_4 and LiCl materials in this method. This was done by placing 20 g of potassium borohydride containing KBH_4 94% into a three-neck flask. The flask was equipped with a condenser, agitator, and thermometer as a suspension in 200 cc of tetrahydrofuran and was freed from peroxide by distillation over sodium. Then, 23 g of 80% technical lithium chloride was added (the impurity consists mainly of potassium chloride and water). A cooling water stream was used to keep the mixture temperature in the 20°C region and agitation maintained for 8 hours [35].

The key points obtained from this method include:

- This method is a process for producing a solution of lithium borohydride in an inert solvent. The selected alkali metals consist of sodium and potassium with excess lithium salt which is soluble in the solvent vent. To effect double decomposition, the lithium salt was chosen so that the alkali metals salt formed by the double decomposition was slightly soluble in the solvent. The process consists of:
 - a. Concentration of the resulting solution by partial evaporation of the solvent so that the lithium salt can be separated.
 - b. By partial evaporation of the solvent, the objective was to separate most of the lithium salt, free the resulting solution from the insoluble material contained in it and recover lithium borohydride from the resulting solution.
- The process of producing a solution of lithium borohydride in a solvent was selected from the group consisting of tetrahydrofuran and formal glycols [35].

2.5.3. Lithium Boron

Filby, et al. (1977) reacted lithium borate, water, and hydrogen chloride. The product of lithium chloride and boric acid was separated by a separator. The function of the separator was to separate the sodium borohydride product from the by-products of sodium methoxide and sodium

borohydride. Boric acid was reacted with methanol to produce an intermediate in the form of methyl borate. A hydrogen source was needed to get hydrogen into the recycling system. Hydrogen was reacted with sodium to produce sodium hydride which has been reacted with methyl borate. The result was reacted with lithium chloride to give the final product, i.e. lithium borohydride and the desired sodium chloride. Lithium borate was recycled into lithium borohydride by reacting lithium borate, hydrogen chloride, and water to produce boric acid and lithium chloride. The resulting lithium chloride and boric acid were converted to lithium borohydride via an intermediate methyl borate [36].

2.6. Electrosynthesis

Electrosynthesis is considered as an effective and efficient synthetic method. When using electrons as reagents, the number of work steps is reduced compared to conventional thermal processes. The resulting reaction of mixture is cleaner, the product isolation is simpler, and the pollution caused using the chemical is reduced [37]. The most common strategy for electrosynthesis is potentiodynamic cycle between a predetermined potential limit and a working electrode in a support electrolyte containing metal ions (M^{n+}) and ferrocene species [38].

In chemical synthesis, the main reaction does not occur spontaneously under initial conditions. Usually, the high activation energy of a process is one of the critical obstacles that has been studied. The use of a catalyst to reduce the activation energy of a chemical reaction usually requires high temperatures. One way to overcome this limitation is to use alternative methods such as electrochemical methods. This is caused by reactions that occur in mild conditions. The main products were obtained with a more environmentally friendly approach [39,40].

Electrochemical technology can be used to replace toxic or hazardous oxidizing/reducing reagents as well as for the in-situ production of unstable and hazardous reagents [37].

2.6.1. $BO(CH_3)_3$, H_2 , and $LiClO_4$

Omweri (2019) synthesized $LiBH_4$ through the electrosynthesis method. The material used was $B(OCH_3)_3$. The equipment used was a potentiostat (PAR 273A) connected to a specially constructed electroanalytic cell containing: a Teflon cell body, thin palladium foil as a working electrode (WE), a platinum coil as an electrode counter (CE), a silver wire as a pseudo reference electrode (RE), and pipe connection [41].

Electrosynthesis shows the electrochemical combination of H_2 and TMB which produces trace amounts of borohydride as a product of electrolysis. The electrochemical activity that observed in Pd foil with TMB underwent a tremendous increase. The products analyzed from single compartment cells did not show sufficient evidence for borohydride formation [41].

The Nafion membrane did not completely separate the reagent electrodes, but analysis of the contents of the cathode compartment with IR confirmed the formation of compounds containing very low concentrations of B–H bonds. IR stretch band 2140.32 and 2078.76 cm^{-1} . The proton spectrum of the NMR did not show the formation of a B–H bond significantly. However, on the closer examination, the spectrum shows some chemical shifts of -0.7, -0.92, -0.94, and -0.97 ppm. This chemical shift corresponds to the value for the chemical shift of commercial BH bonds containing lithium borohydride-like compounds. Dry reagents can provide evidence of

borohydride formation via electrosynthesis methods. A more suitable solvent was one containing lithium borohydride [41].

Conclusion

LiBH₄ is a promising material in technology development, especially as a hydrogen storage material. The production of LiBH₄ materials can be done through the ball milling, chemical treatment, electrosynthesis, impregnation, and nanoconfinement method.

The ball milling method is a method that is often used and is the best candidate in the synthesis of LiBH₄. This is due to the process of synthesizing nanoscale particles which are very useful in the application of LiBH₄ materials, especially in the manufacture of hydrogen storage.

The starting materials used are very diverse in which compounds can be derived from waste or from others that can form LiBH₄. The best starting material is LiBH₄ commercial and mesoporous carbon as the results obtained are nano-LiBH₄/ C_{mesoporous} has nanoscale-size with a diameter of 5 nm and the desorption value is lower than LiBH₄ bulk. This is thermodynamically advantageous and the product is thermally stable. However, nano-LiBH₄/ C_{mesoporous} is difficult to identify by XRD.

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