

**THERMALLY SINTERED ALUMINUM COMPOSITES WITH
LOW MELTING POINT METALS FOR HYDROGEN
PRODUCTION THROUGH WATER SPLITTING REACTION**

BY

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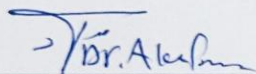
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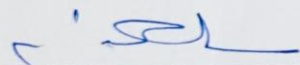
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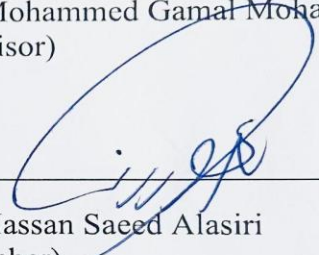


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Dedication

I dedicate this work to my family

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I express my deep and sincere gratitude to the Almighty for granting me the wisdom and strength to undertake this thesis project.

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List of Abbreviations

X-ray Diffraction	XRD
Differential Scanning Calorimetry	DSC
Scanning Electron Microscope	SEM
Thermogravimetric Analysis	TGA
Energy Dispersive Spectroscopy	EDS
Aluminium	Al
Gallium	Ga
Indium	In
Tin	Sn
Liquid Metals	LM
Eutectic	E

Abstract

Full Name : Md Hasan Shahriar Raby

Thesis Title : Thermally Sintered Aluminum Composites with Low Melting Point Metals for
Hydrogen Production Through Water Splitting Reaction

Major Field : Chemical Engineering

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This study investigates aluminum activation by thermal sintering using liquid metals (gallium, eutectic Ga-Sn alloy, and eutectic Ga-Sn-In alloy) as activating agents for hydrogen production via water splitting reaction. Aluminum foils are sprayed with liquid metal particles then thermally sintered to produce aluminum composites that react spontaneously with water at ambient conditions to produce hydrogen. Composites of aluminum with gallium react very slowly (10-20 hours) with water at high temperature ($\sim 70^\circ\text{C}$). Interestingly, the reaction of aluminum composites with eutectic alloys of Ga with Sn and Sn-In is extremely fast (3-18 minutes) in comparison to those with Ga metal. Aluminum composites with Ga-Sn achieved a very high reaction rate with an intermediate yield, while the composites with Ga-Sn-In achieved a higher yield at a slower rate. Hydrogen yield increases with the increase of liquid metal ratio in aluminum composites with Ga and Ga-Sn, and plateaus after a specific ratio. However, hydrogen yield from aluminum composites with Ga-Sn-In significantly decreases with the increase in the liquid metal ratio due to the formation of In-Sn intermetallic compounds that prevent Sn and In from participating in the water splitting reaction. The reaction rate is highly dependent on reaction temperature, for instance increasing the reaction temperature by 20°C leads to reducing the reaction time from 65 minutes to 10 minutes. The composites have a very long shelf life and retain more than 70% of their activity after storage for three months in ambient conditions.

ملخص الرسالة

الاسم الكامل: محمد حسن شهريار راوي
عنوان الرسالة: مركبات الألمنيوم المتبلدة حرارياً مع معادن منخفضة درجة الانصهار لإنتاج الهيدروجين عبر تفاعل تحليل الماء
التخصص الرئيسي: الهندسة الكيميائية
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تبحث هذه الدراسة في تنشيط الألمنيوم عن طريق التليد الحراري باستخدام المعادن السائلة (Ga ، وسبيكة Ga-Sn الأيوتكتيكية، وسبيكة Ga-Sn-In الأيوتكتيكية) كعوامل تنشيط لإنتاج الهيدروجين من خلال تفاعل انشطار الماء. يتم رش رقائق الألمنيوم بجسيمات من المعادن السائلة، ثم تُلبد حرارياً لإنتاج مركبات من الألمنيوم تتفاعل تلقائياً مع الماء في الظروف المحيطة لإنتاج الهيدروجين. تتفاعل مركبات الألمنيوم مع الجاليوم ببطء شديد (من 10 إلى 20 ساعة) مع الماء عند درجات حرارة مرتفعة (~70 درجة مئوية). ومن المثير للاهتمام أن تفاعل مركبات الألمنيوم مع السبائك التكتيكية من Ga-Sn و Ga-Sn-In يكون سريعاً للغاية (من 3 إلى 18 دقيقة) مقارنةً بتلك التي تحتوي على Ga فقط. وقد حققت مركبات الألمنيوم مع Ga-Sn معدل تفاعل مرتفعاً مع عائد متوسط من الهيدروجين، بينما حققت المركبات مع Ga-Sn-In عائداً أعلى لكن بمعدل تفاعل أبطأ. يزداد عائد الهيدروجين مع زيادة نسبة المعدن السائل في مركبات الألمنيوم مع Ga و Ga-Sn، ويصل إلى حد التشبع بعد نسبة معينة. ومع ذلك، فإن عائد الهيدروجين من مركبات الألمنيوم مع Ga-Sn-In ينخفض بشكل كبير مع زيادة نسبة المعدن السائل، وذلك بسبب تكوّن مركبات بينية من In-Sn تمنع Sn و In من المشاركة في تفاعل انشطار الماء. ويعتمد معدل التفاعل بشكل كبير على درجة حرارة التفاعل؛ فعلى سبيل المثال، يؤدي رفع درجة الحرارة بمقدار 20 درجة مئوية إلى تقليص زمن التفاعل من 65 دقيقة إلى 10 دقائق. وتتميز هذه المركبات بعمر تخزيني طويل وتحفظ بأكثر من 70% من نشاطها بعد تخزينها لمدة ثلاثة أشهر في الظروف المحيطة.

Chapter 1: Introduction

1.1 Background Study

Petroleum-based goods are mostly used to meet the energy needs of society and industry today because of their affordable prices, easy accessibility, and effective distribution system. However, the global fossil fuel supplies are finite, and the pollution from exploitation makes the fossil fuel-based energy system unsustainable [1]. The burning of fossil fuels generates toxic substances that negatively impact human health and the environment. Moreover, the world's confirmed supplies and consumption patterns may soon be altered [2], and the rising energy demands have increased prices for conventional fuels, impacting economies dependent on imports. Therefore, future energy sources should be free of carbon emissions and renewable to effectively mitigate climate change and decrease reliance on oil [3,4]. The growing severity of air pollution and the declining availability of fossil fuels are driving mankind to seek out and adopt clean, sustainable energy sources such as solar, hydroelectric, wind, and nuclear power [5–8]. **Figure 1.1** illustrates current energy demand by sources and the contribution of different emitted gases, which come from burning fossil fuels.

Hydrogen has a very high calorific value, with a specific energy of approximately 120 MJ/kg — nearly three times that of gasoline (44 MJ/kg) and diesel (45 MJ/kg). Its high energy density per unit mass makes it an ideal fuel for weight-sensitive applications, such as aviation and fuel cell vehicles [9–11]. Upon combustion with oxygen, hydrogen undergoes a process ($2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$) that yields just water, generating energy without releasing carbon dioxide, which presents a unique benefit over fossil fuels that emit CO_2 . Several ways, including hydrocarbon reforming, photolysis, water electrolysis, hydrolysis, and biomass conversion may generate it [12–16]. Nonetheless, hydrogen possesses poor volumetric energy density, necessitating storage methods

such as pressurized gas tanks (350-700 pressure), cryogenic liquid storage (-253°C), or chemical hydrides. Despite its potential, the obstacles related to hydrogen storage and handling (such as flammability and infrastructure demand) are critical factors influencing its widespread adoption as a sustainable fuel alternative.

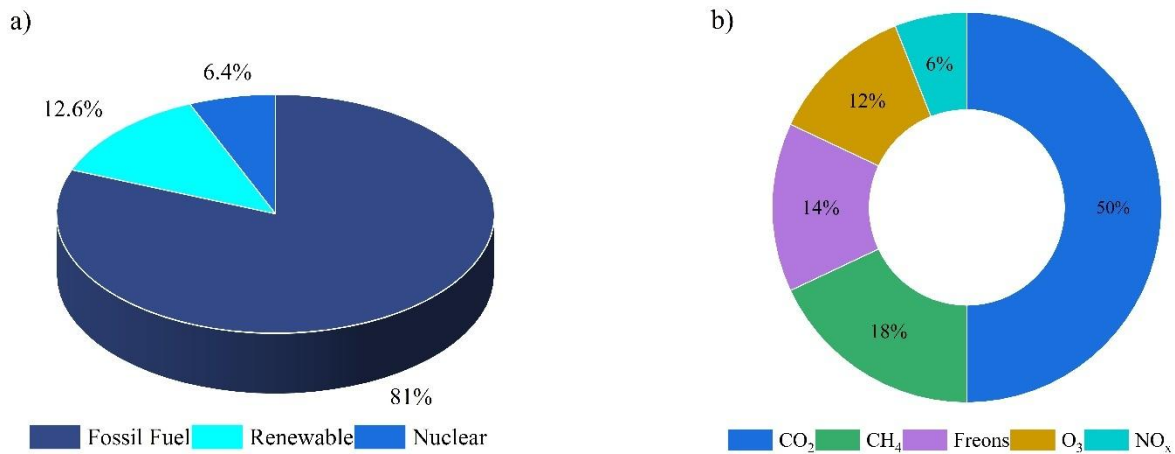


Figure 1.1.: a) Current energy demand by source [17], b) Percentage contribution of different greenhouse gases to the world average temperature increment [18].

1.2 Objectives

- To produce hydrogen through the water splitting reaction using thermally sintered aluminum composites with gallium metal, gallium-tin, and gallium-tin-indium liquid metal alloys, and to study the factors affecting the volume and rate of hydrogen production as well as hydrogen yield, including:
 - The mass ratio of Ga: Al, EGaSn: Al, and EGaSnIn: Al.
 - The reaction temperature.
 - The storage time of the composites.
- To understand the role of activating agents in composites and the reaction mechanism for the water splitting reaction by analyzing the composites before and after they react with water.

Chapter 2: Literature Review

2.1 Hydrocarbon Reforming

Hydrocarbon reforming is a process that breaks down hydrocarbons to produce valuable products such as hydrogen and usable fuels. It often takes place through the catalytic reaction of hydrocarbons with steam. This technique is crucial for hydrogen production, extensively utilized in industries and sustainable energy technologies, such as fuel cells [19]. Three primary techniques for producing hydrogen from hydrocarbons are auto-thermal reforming (ATR), partial oxidation (POX), and steam reforming. Despite the advantages of these methods, there are major drawbacks, such as high toxic air emission rate, high reaction temperature, and process complexity [20,21]. The three methods are discussed in more detail in the coming section.

2.1.1 Steam Reforming

Steam reforming is the process of converting hydrocarbons with steam into a mixture of hydrogen, carbon monoxide, methane, and unreacted steam. Common feedstocks include liquid fuels such as naphtha, and sometimes kerosene, natural gas, and LPG. Among hydrogen production methods, steam reforming is considered the most efficient, owing to its highly endothermic nature, lower operating temperatures compared to partial oxidation (POX) and auto-thermal reforming (ATR) technologies, and its potential to achieve a high H_2/CO ratio [22,23]. Generally, 180°C is required for methanol and oxygenated hydrocarbons during the SR process, whereas over 500°C is needed for most conventional hydrocarbons [24,25]. Furthermore, J. Liu et al. provide a summary of diverse catalysts utilised in the catalytic steam reforming of aromatic hydrocarbons for generating hydrogen [26]. This process with additional water gas shift reactions of heptane and methane are illustrated below [21,27] .



The procedure involves two primary parts. The hydrocarbon feedstock is introduced into a tubular catalytic reactor together with steam [28]. Syngas, or an H_2/CO gas mixture, is produced during this process with a reduced CO_2 percentage equations (1) and (2). Oxygen or air is added to the reactor feed to burn a portion of the hydrocarbon to produce heat and allow the mixture to reach the necessary reaction temperature. The low-temperature product gas is introduced into the carbon monoxide (CO) catalytic converter, where steam significantly transforms CO into H_2 and CO_2 (3). To prevent catalyst poisoning, the feed to the steam reforming reactor must be free from sulfur-containing chemicals [29].

Active catalysts in steam reforming processes are often transition metals like nickel (Ni) and cobalt (Co) or noble metals such as platinum (Pt), palladium (Pd), rhodium (Rh), and ruthenium (Ru) [28,30–34]. When the noble metals (Rh, Ru) were compared to nickel catalysts, they demonstrated significantly greater activity and reduced coke production considerably [35–37]. Nonetheless, non-noble metal catalysts are attractive for applications at large scales owing to their reduced cost, widespread availability, and elevated activity. In extreme reaction conditions, they exhibit reduced resistance to cooking, phase transition, and sintering. Carbonaceous deposits accumulate more rapidly on non-noble metals compared to noble metals due to an accumulation of active component particles, which concurrently diminishes the concentration of surface-active sites [34,38]. As a result, over time, on stream, the catalyst deactivation is observed. Therefore, synthesizing effective, reliable, and affordable catalysts to produce hydrogen using hydrocarbon fuel reforming is a big challenge. Based on Higher Heating Values (HHV), methane steam reforming is regarded

as one of the most widely used industrial methods for hydrogen production, capable of achieving thermal efficiencies of up to 85% [39].

Moreover, the ethanol steam reforming for hydrogen production can be explored because substantial catalyst research has been undertaken. the most often researched ethanol steam reforming (ESR) catalysts are Rh [40,41] and Ni [42] based catalysts, which have a very high selectivity toward hydrogen generation. Al₂O₃ [43,44], MgO [45], ZrO [46], CeO₂ [47], La₂O₃ [48], Nb₂O₅ [47], perovskites [49,50], and bi-metallic [49,51] were used as support materials for the catalyst. The excellent C–C bond cracking ability of the Rh catalyst resulted in a substantial H₂ yield when the Rh/CeO₂ catalyst was employed for ESR at 400 °C [41]. Additionally, Ni/BZCY₇ (BaZr_{0.1}Ce_{0.7}Y_{0.2}O₃), Ni/BZCYYb (BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O₃), and Ni/BZCY₄ (BaZr_{0.4}Ce_{0.4}Y_{0.2}O₃) on perovskite supports were shown to have reduced carbon deposition and greater catalytic activity compared to other oxide catalysts [50]. Moreover, with their oxide on various supports, Cu and Zn have been utilized to produce H₂ from methanol. Sengodan et al summarized the different catalysts used for ESR [52]. Cu_xMn_{3-x}O₄ spinel has provided the best performance for conversion [49].

2.1.2 Partial Oxidation

Partial oxidation (POX) is a process where hydrocarbons react with a smaller amount of oxygen than what would be needed for full combustion and release heat. Some examples of partial oxidation reactions are shown in Equations 4–6 [22,52]. Research has shown that the efficiency of the POX method is lower than that of the steam reforming process and that its extensive usage of pure oxygen results in high operating costs [53].





The most researched POM catalysts include noble metals, perovskite oxides, and supported transition metals (Ni, Co, and Fe) [54]. These catalysts are comparable to those used in steam reforming. While transition metals are important components of POM catalysts, methane conversion is mainly dependent on metal species with varying oxidation states. Metallic nickel encourages syn-gas production, whereas Ni species with an oxidation number of at least two encourage methane to burn completely. The support and the synthesis method feature to determine the order of dispersion of metallic catalyst species. According to Choi and Moon, Co/ZrO₂ is a remarkably cost-effective catalyst exhibiting excellent conversion and hydrogen selectivity compared to other catalysts [55]. According to another study on single oxide-supported catalysts, carbon is produced only on these catalysts, such as Ni/La₂O₃ and Ni/CeO₂, rather than on composite supports like CeO₂-La₂O₃ [56]. Additionally, it was stated that the defective species play a significant part in the POM over the support [57]. Moreover, researchers have found that perovskite-based catalyst materials offer excellent stability, strong catalytic activity, and good resistance to carbon buildup during POM. They studied by using reactive oxygen species to prevent carbon from accumulating on the surface, effectively lowering the risk of carbon deposition, and in some cases, even stopping it altogether. This implies that carbon deposition may be successfully decreased using perovskite catalysts [52].

2.1.3 Autothermal Reforming

Auto-thermal reforming (ATR) is a combined combustion and catalytic process carried out in an adiabatic reactor. The system typically includes a catalyst bed, a combustion chamber, and a burner, all housed within a pressure shell lined with refractory material. In ATR, partial oxidation of methane produces carbon monoxide, hydrogen, and additional feed for steam reforming, which

reduces overall energy consumption [58]. According to the "mixed is burnt" approach, the combustion zone of an ATR functions as a turbulent diffusion flame where oxygen and hydrocarbons mix and burn quickly and exothermically. Methane combustion in the flame zone proceeds towards CO and H₂O formation at an O₂/CH₄ ratio of 1.5, with a sub-stoichiometric overall oxygen-to-hydrocarbon ratio (0.55-0.6). The temperature within the combustion chamber varies from around 1100 to 1300°C adjacent to the catalyst bed and exceeds 2500°C at the flame core. Gas-phase processes with slower kinetics, such as carbon monoxide oxidation and methane steam reforming, occur in the thermal zone thereafter but do not reach equilibrium [35]. A specific goal, such as achieving a high hydrogen yield with low carbon monoxide levels, directly influences the operational conditions, like temperature and pressure.

Although an endothermic process requires energy input, steam reforming may attain high hydrogen efficiency and a low proportion of carbon monoxide. ATR generates more hydrogen than POX and may be rapidly reduced in output and reactivated [58]. In the auto-thermal process, it is widely recognized that regulating the steam-to-carbon ratio and oxygen-to-fuel ratio is crucial for sustaining an appropriate temperature and averting coke formation [59–61]. Moreover, because of its favorable gas composition, compactness, decreased capital expenditure, and the possibility of economies of scale, ATR is attractive to the "Gas to Liquid" fuel industry [21]. The thermal efficiency of methane partial oxidation (POX) is lower than that of steam reforming because of greater heat losses during the POX process. Moreover, the ATR process with the right catalysts, hydrogen may be produced on board for usage in cars from gasoline and other higher hydrocarbons [62].

2.2 Biomass-based Hydrogen Production

Energy crops, agricultural residue (livestock and harvest waste), industry and municipal trash, and forestry waste (cutting down land and harvesting trees) are the four primary categories of biomass sources with high energy production potential. Energy crops are fully developed regarding energy content; agricultural residue comprises livestock and harvest waste; forestry waste results from clearing land and harvesting trees [63]. The mass percentage of H element in biomass is about 6%, so 1 kilogram of biomass will yield 0.672 m³ of gaseous hydrogen or over 40 percent of the biomass's total energy [64]. Traditional methods for producing hydrogen from biomass include gasification, pyrolysis, and converting biomass into liquid fuels through processes like hydrolysis, liquefaction, supercritical extraction, and others — often followed by reforming techniques such as steam reforming, partial oxidation (POX), or auto-thermal reforming (ATR) [65]. Gasification of biomass, a thermochemical process conducted in a controlled oxygen-deficient environment at high temperatures (700–1000 °C), and biomass pyrolysis, a thermochemical process that thermally decomposes organic materials (300-700 °C) in the lack of oxygen, both provide hydrogen. Gasification produces a blend of hydrogen, nitrogen, and carbon monoxide, whereas pyrolysis yields methanol, coke, and other gases [66]. Biomaterials can be gasified at high temperatures, condensed into pyrolysis oils, and then reformed to produce hydrogen. Among these methods, biomass gasification is considered more efficient for producing syngas (a mixture of H₂ and CO) compared to pyrolysis. This is because gasification occurs at higher temperatures and in the presence of an oxidizing agent, resulting primarily in gaseous products rather than liquids or solids [67,68].

By dry mass, 12 ± 17% of hydrogen has been produced using this process [69]. In a research conducted by Akubo et al., six biomass materials were analyzed using a fixed-bed two-stage

reactor: cotton stalk, rice husk, wheat straw, sugarcane, coconut shell, and palm kernel shell. Catalytic steam reforming and pyrolysis of pyrolysis oil were also investigated. The findings revealed a notable enhancement in gas production and increased hydrogen composition in syngas when steam with a 10 wt.% nickel-based alumina catalyst (NiAl_2O_3) was utilized. The hydrogen yield for pyrolysis-catalytic steam reforming at 550°C and 750°C ranged from 16.38 mmol/g to 25.35 mmol/g, whereas the hydrogen yield for solo pyrolysis of wheat straw at 550°C varied from 5.81 mmol/g to 6.77 mmol/g [70]. The thermal decomposition of biomass produces a complex mixture of oxygen-rich compounds, commonly known as bio-oil [71], which includes anhydrous sugars, alcohol, ketones, carboxylic acids, and aldehydes [72]. Bio-oil has been synthesized to generate hydrogen, which may be used as a fuel in the future. However, the process is difficult because of the variety of components, high coke formation, and intricate reaction network of bio-oil [73]. Chong et al. summarize various operational parameters. The catalytic activity of SR of these oils includes temperature, the steam-to-carbon (S/C) ratio, pressure during the reaction, metals employed, kinds of catalytic supports, and gas hourly space velocity (GHSV). They also reported using various industrial effluents (e.g., Palm Oil mill effluent, Cheese whey wastewater, Olive mill wastewater) to produce H_2 with suitable reaction conditions [74]. Valle et al.'s investigation used a $\text{Ni/La}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst to convert crude bio-oil to H_2 -rich gas. This gas is produced by the two-step (thermal + catalytic) technique used in the SR of raw bio-oil. 93% H_2 is created at 700°C and 0.38 g catalyst. h/g bio-oil [75].

In biomass steam gasification, raw biomass is heated to elevated temperatures, breaking it down to produce a mix of combustible gases such as hydrogen (H_2), methane (CH_4), carbon monoxide (CO), and other hydrocarbons. This reaction uses steam as the primary gasifying agent. The amount of hydrogen in the produced syngas is influenced by factors like the characteristics of the

biomass, the reaction temperature, and the ratio of steam to biomass [76]. For the formation of hydrogen-rich syngas by carbon gasification, methane reforming, water-gas conversion, and hydrocarbon reforming, steam is widely regarded as the most appropriate gasification mediator. Additionally, supercritical water gasification is a hydrothermal method that produces hydrogen, carbon dioxide, methane, and various gases by breaking down biomass in a liquid water processing medium. Here, water serves as both a reactant and a reaction medium in methanation, steam reforming, and water-gas conversion [77]. which drastically lowers energy consumption by eliminating the need to dry raw materials before gasification [78]. Biomass gasification frequently uses alkali catalysts such as NaOH, KOH, KHCO₃, K₂CO₃, Na₂CO₃, and Ca(OH)₂ [79]. The formation of hydrogen can also be catalyzed by a range of metals and oxides, such as pyrolytic carbon, combined iron slag, and catalysts based on nickel [80]. Natural minerals such as olivine and dolomite catalyze biomass gasification [81]. However, further scientific advancements are still needed for biomass hydrogen generation based on current technology to make it ecologically sound and economically competitive for substantial industrial production [82].

2.3 Water Hydrolysis

2.3.1 Electrolysis

Electrolysis is a common method for producing hydrogen (H₂) and oxygen (O₂) by splitting water (H₂O) using electricity. The process takes place in an electrolyzer, which contains two electrodes — a cathode and an anode — submerged in water. When a direct current (DC) is applied, water molecules at the cathode are reduced to release hydrogen gas, while at the anode, water molecules are oxidized to produce oxygen gas. The anodic reaction is:



The cathodic reaction is:



The efficiency of electrolysis depends on several factors, including the type of electrolyzer, the applied voltage, and the quality of the water used. In industrial settings, electrolysis is often powered by renewable energy sources such as solar or wind, making it a sustainable and environmentally friendly method for hydrogen production [83,84]. The electrolysis process can be categorized into three sub-sections based on the electrolyzer types.

2.3.1.1 Proton Exchange Membrane (PEM) Electrolysis

PEM electrolysis employs a solid polymer membrane as the electrolyte, with a proton-conductive membrane positioned between the anode and cathode [85]. Water molecules are split at the anode into electrons, protons, and oxygen (O_2). The protons travel across the membrane, combining with electrons to produce hydrogen (H_2) at the cathode. This process depends on highly efficient catalysts, with platinum (Pt) commonly used at the cathode and iridium (Ir) at the anode. The catalyst layers are either embedded within the membrane or applied to porous gas diffusion layers on both sides of the PEM. These porous materials, usually carbon or metal, ensure efficient gas transport and manage water effectively [86,87]. Researchers are investigating less expensive alternatives to the noble metals used in PEM electrolyzers, such as iridium (Ir) and platinum (Pt). Researchers are exploring iridium alloys combined with additional metals, such as ruthenium or cobalt, transition metal compounds like phosphides (e.g., NiP, CoP) and nitrides (e.g., MoN). The goal of using these materials is to reduce dependence on expensive metals while increasing the active surface area of the catalysts at the cathode to enhance the hydrogen evolution reaction (HER). For the oxygen evolution reaction (OER), researchers are developing multi-metallic alloys to boost catalytic activity, improve stability, and make the process more cost-effective [88,89].

This process is highly efficient, with energy conversion efficiencies between 60-80%, and can operate at relatively low temperatures (around 50-80°C). The typical range for current density is 1 to 2 A/cm², the voltage is 1.8-2.2 V, and the pressure is maintained at 1 to 30 bar [90]. They are also compact, making them suitable for smaller, decentralized applications. The pure hydrogen produced (up to 99.99%) makes PEM suitable for high-purity fuel cell applications. PEM electrolysis is powered by renewable electricity sources, such as wind or solar, to ensure hydrogen is sustainably produced. However, they are more expensive and less scalable than alkaline electrolysis due to the high cost of precious metal catalysts and materials, and the requirement of ultra-pure water to prevent membrane fouling.

2.3.1.2 Alkaline Electrolysis (AE)

Alkaline electrolysis employs a solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) as the electrolyte to divide water into hydrogen and oxygen using electricity. The electrodes, typically made from nickel-based materials, facilitate the reaction, with catalysts like nickel or cobalt boosting efficiency at the anode [91]. Research is now focused on Nickel-Iron (NiFe) and Nickel-Cobalt (NiCo) alloys [92,93], transition metal oxides (such as MnO₂ and Co₃O₄), and layered double hydroxides (LDHs) to improve OER performance [94,95]. Furthermore, manganese (Mn) and molybdenum (Mo) based catalysts are refined for cost-effectiveness and high accessibility [96,97]. The operation range of temperature is 60-90°C, current density is 0.2 to 0.5 A/cm², voltage is 1.8 and 2.4 V, and pressure is up to 30 bar. Alkaline electrolysis systems are more cost-effective than PEM systems because of the minimal cost of materials and catalysts. The efficiency is also between 60-80%, though the systems are larger and less efficient in energy conversion when compared to PEM systems [98,99]. Alkaline electrolyzers are highly scalable, appropriate for large-scale industrial applications, and capable of producing

hydrogen in the range of high purity (around 99.5-99.9%). They are commonly powered by grid electricity, including renewable or conventional sources. The main limitation is their slower response time and the potential for lower-purity hydrogen due to impurities in the electrolyte or the electrodes.

2.3.1.3 Solid Oxide Electrolysis (SOE)

Solid oxide electrolysis (SOE) works at high temperatures (700-1000°C) using a solid oxide ceramic material as the electrolyte [100]. This method is frequently combined with heat sources to enhance efficiency, as elevated temperatures lower the electrical energy requirement for water splitting [101]. In the cathode, nickel and yttria-stabilized zirconia (YSZ) composites are used for the hydrogen evolution reaction (HER) [102,103]. These materials provide excellent conductivity and catalytic activity. In the anode, perovskite materials (e.g., strontium-doped lanthanum manganite or cobaltite, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) facilitate the oxygen evolution reaction (OER) [104,105]. In addition, materials that combine oxides with metals are now intended to be applied to improve activity and durability under high-temperature conditions. Current research has also emphasized innovations in protective layers and coatings for prolonged operation to prevent sintering and degradation [106,107]. SOE systems offer high efficiencies, often exceeding 80%, because they can utilize electrical and thermal energy. The operation temperature is 700-1000 °C, current density is 0.3 to 1 A/cm², voltage is 1.1 to 1.3 V, and pressure is at near-atmospheric pressure, though pressurized systems may integrate with downstream hydrogen storage. They also have the potential for large-scale production, but scalability is currently limited due to the technical challenges associated with materials that can withstand high temperatures. The hydrogen produced can be high purity (up to 99.9%), though contaminants from the materials used for the reaction environment could affect purity. It can be co-electrolyzed with steam and CO₂ to produce syngas

(H₂ and CO), a precursor for synthetic fuels [108–111]. SOE electrolysis is typically powered by excess renewable energy or waste heat, making it an attractive option for integrating into industrial processes with significant thermal outputs, such as those in the chemical or steel industries. However, it requires significant time to reach operating temperature, limiting flexibility for intermittent renewable energy use.

In summary, PEM and alkaline electrolysis are commonly used for hydrogen production, each with distinct cost, scalability, and efficiency advantages. PEM is more efficient and produces higher purity hydrogen but is less scalable and costly. Alkaline electrolysis is more scalable and cost-effective, though with slightly lower efficiency. While still in development, solid oxide electrolysis offers high efficiency and is promising for large-scale applications with integration into heat-intensive industries. **Table 2.1** compares different aspects of the three electrolysis techniques.

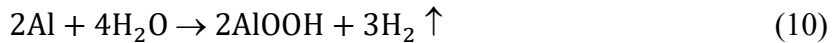
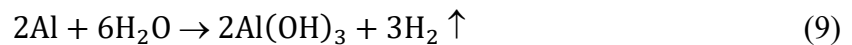
Table 2.1 Comparison of various electrolysis processes

Method	Catalysts	Efficiency	Hydrogen Purity	Scalability	Ref.
PEM	Precious metals (Pt, Ir)	80% - 90%	>99.9%	Limited	[86,90]
AWE	Non-noble metals (Ni, Co)	60% - 80%	Up to 99.9	High	[91,99]
SOE	Non-noble metals (Ni, Ceramic)	90% - 100%	Up to 99.9	Limited	[103,104]

2.3.2 Reaction with Aluminum

Aluminum is one of the most plentiful metals on Earth and is valued for its remarkable properties. It offers excellent ductility, impressive hardness, high electrical and thermal conductivity, strong reflectivity, low density (2.7 g/cm³), and excellent corrosion resistance [112]. Aluminum hydroxide and hydrogen gas can be generated by aluminum reacting with water according to stoichiometric equations (9) and (10) [16]. However, this reaction is usually hindered by a passivating oxide layer that forms on the aluminum's surface, avoiding further interaction with water. Despite this challenge, the spontaneous reaction of aluminum with water holds great potential for hydrogen production. It offers a safe, cost-effective, and efficient way to use water as a hydrogen carrier, which is abundant and easy to handle. This reaction does not require catalysts, extreme conditions, or electrical input, making it a straightforward and sustainable approach.

An "aluminum activation" process enhances aluminum's reaction with water. This process prevents the formation of the passivating oxide layer or creates defects in it, allowing the reaction to proceed more effectively. Aluminum activation can be achieved through various methods, including alloying it with other metals to disrupt the oxide layer and promote reactivity [112–114], milling with salt and oxide powder [115–117], employing alkaline electrolytes [112,118], or raising the reaction temperature [119].



2.3.2.1 Activated Aluminum Composites Synthesis Methods

This section reviews various activated aluminum composite synthesis methods, such as ball milling, alloying, and gas atomization.

Ball milling, often referred to as mechanical ball milling, is a large-scale, low-cost, and straightforward preparation technique that involves squeezing and impacting material particles with milling balls to create tightly integrated substances [120,121]. Due to aluminum's high flexibility, the ball milling causes the aluminum particles to bond. In contrast, the milling balls cause imperfections, displacements, and fractures in the distorted aluminum particles, raising their specific surface area and depleting the initial thick alumina film [122–124]. Ball milling improves the reactivity of aluminum by allowing additives to stick to the outer surface of aluminum particles and penetrate their interiors, producing surface grooves. During hydrolysis processes, these defects expand the reaction area [112,122,125–127]. The morphology and reactivity of aluminum powders are greatly affected by ball milling conditions such as milling time, ball size, weight, and milling speed. Because of aluminum's ductility, longer milling durations reduce particle size, whereas shorter milling times do not produce enough deformation [127,128]. Optimizing milling conditions is crucial for controlling the reactivity of aluminum. Research by Razavi-Tousi et al. examined how the milling duration impacts the efficiency of aluminum-water reaction, the yield of hydrogen gas, and the morphology of aluminum powder. Their findings showed that milling can create fresh reactive surfaces and reduce particle size. However, the internal multilayered structure of aluminum particles can be disrupted by excessive milling, which reduces their hydrogen production efficiency [129]. Another study focused on how soluble salts affected aluminum's ability to produce hydrogen in water interactions. It was discovered that ball milling may reduce the crystal grain size of the aluminum composite [117] and it may also improve hydrogen production capability by evenly dispersing soluble salts in activated aluminum particles [130].

Alloying is another mechanism to produce aluminum composites. By melting and solidifying different metals, the alloying process makes it possible to alloy aluminum with other metals efficiently, greatly increasing its water reactivity [131,132]. An et al. asserted that a reduction in grain size causes a greater number of aluminum atoms to get involved in the hydrolysis reaction by reducing the distance for the diffusion between aluminum atoms and the reaction spot, which was proved by utilizing Bi-containing five-element Al, Ga, Sn, and In alloys [133] which was also further proven by Wang et al [134]. Moreover, to increase the alloy's specific surface area during the water reaction, Cu can be added to stop the formation of Al crystal grains [135]. According to a study, when a small amount of titanium is present in an aluminum alloy with a columnar grain structure, it inhibits the interaction of aluminum with water and decreases hydrogen production efficiency. On the other hand, when the titanium content in the alloy increases, the rate at which aluminum and water react rises, and the grains of aluminum are equiaxed, which is the cause of higher hydrogen yield [136]. Furthermore, the temperature and duration of the heat treatment process will impact the activated aluminum composite's water reactivity [137]. Furthermore, incorporating carbon material with aluminum can hasten the disintegration of composite particles and raise their reactivity [138].

Alkaline solutions, such as potassium and sodium hydroxides, react with aluminum to reduce the oxide layer and speed up hydrolysis [139–141]. Waste aluminum foil may produce hydrogen without further ball milling in the presence of the 0.75N NaOH solution and Bi additives, whereas 0.75 KOH can produce hydrogen without any further additives [142,143]. On the other hand, the hydrolysis process of aluminum can be accelerated by choline hydroxide, which will reduce the fluctuation of hydrogen production [144]. The water reaction efficiency of aluminum can be enhanced in alkaline solutions, including CaO or Li/Li₂O, in deionized water [145].

Using a high-pressure gas flow, the gas atomization process breaks down molten liquid metal or alloy into tiny beads smaller than 150 μm in diameter. This method can thoroughly damage the passive layer on the aluminum surface, allowing the aluminum to mix with the additional metal [146]. The 80Al-10Bi-10Sn wt.% composite particles exhibit a unique core-shell structure with numerous surface fractures [50]. In contrast, Al-20%Sn powder features evenly distributed Sn along the grain boundaries, while Al-20%Bi powder creates a partial core-shell structure, which makes a cluster on the surface with Bi [140]. Despite their high oxidation resistance, powdered aluminum alloys can react vigorously with distilled water.

The aluminum-water reaction kinetics are significantly influenced by trace amounts of organic acids and fluoride ions, while other cations and anions have minimal impact. These acids and fluoride ions interact with Al-OH groups on the surface of aluminum particles, forming complexes that slow down the hydration of the oxide layer. This, in turn, extends the initiation time of the reaction [147]. From the above discussion, it can be illustrated that by improving the mixture of catalyst and aluminum powder, the ball milling technique creates an aluminum composite particle with several layers that increase the hydrogen production rate.

2.3.2.2 Additives to activated aluminum

The reactivity of activated aluminum with water can be enhanced by incorporating low-melting-point metals such as bismuth (Bi), tin (Sn), mercury (Hg), indium (In), and gallium (Ga), as well as compounds like sodium chloride (NaCl) and calcium hydride (CaH_2). Adding Bi and Sn significantly improves aluminum's interaction with water compared to zinc (Zn), calcium (Ca), or Ga. At normal ambient temperatures, liquid metals like Ga and Hg can penetrate and interrupt the oxide layer on aluminum particles, activating the surface. Aluminum also forms corrosion sites with mercury or zinc amalgams, breaking down the oxide coating. Mercury, in particular, dissolves

aluminum, allowing it to react with water at the mercury-water interface, rapidly producing hydrogen. This process continues as aluminum dissolves into the zinc or mercury amalgam film, sustaining hydrogen production [148,149]. At room temperature, the hydrolysis reaction rate of the Al–Bi alloy is faster than that of the Al–Sn alloy. Ternary composites have attracted considerable interest owing to their distinct benefits. These composites utilize two activation metals, which often work synergistically to enhance aluminum deformation during ball milling and boost hydrolysis activity. The activation process in ternary composites results in nonreactive binary phases that exhibit high hydrolysis efficiency. This improved performance is partly attributed to developing intermetallic phases (IMFs) between specific activation metals [150]. Additions of Zn and Ga to the Al–Bi alloy in the milling process speed up the hydrolysis reaction, but including other metals (Sn, In, and Mg) had the opposite effect. Al-5Bi-10Ga-5Zn produced a maximum of 940 ml of hydrogen per gram. However, Zn showed an inverse relationship with Bi. Higher Zn content with lower Bi reduced the hydrogen generation capacity of this alloy [151]. When aluminum alloys are prepared by planetary ball milling with Ga, In, and Sn, Ga-Sn does not react with tap water at ambient temperature if the alloying elements have a weight ratio below 10 percent. Al-In-Sn and Al-Ga-In alloys, however, can react with tap water under normal conditions. The performance of the quaternary Al-Ga-In-Sn alloy outperforms that of the ternary-activated Al alloy [152]. Moreover, the reactivity of Al–Bi–hydride or salt mixtures during ball milling is boosted by three main factors: the reduction of the mixture’s average particle size, the exothermic dissolution of additives like MgH_2 and MgCl_2 , and the formation of micro-galvanic cells within the Al–Bi alloy [153]. Pitting corrosion on the passivation layer also promotes hydrolysis due to the addition of chloride ions [154]. As a result, NaCl addition benefits improved hydrolysis characteristics of aluminum alloys with a lower hydrolysis temperature, faster kinetics, and greater

efficiency [116,155]. For the Al-10 wt.%Bi (OH)₃-5 wt.% NaCl system in water hydrolysis, alumina prevents agglomeration between Bi-Bi, Al-Bi, and Al-Al during the milling process, bismuth forms micro-galvanic cells, and chloride ions facilitate aluminum corrosion during hydrolysis, which provides 1000 mL/gm hydrogen gas [156]. By doping Al-In-NaCl alloys with Zn and Ga, their reactivity may be enhanced at ambient temperature, leading to a greater yield. Adding cadmium to Al-Hg alloys makes them less reactive [116]. By adding CaH₂, hydrogen production was optimized to 1050 ml/gm. Liu et al. have examined the effect of milling conditions and reaction temperature on the efficacy of aluminum hydrogen generation. It was found that an increase in CaH₂ concentration and milling duration resulted in a reduction of aluminum grain size and the degradation of the protective oxide layer on the Al powder's surface. The corrosion of aluminum is intensified, and the hydrolysis of CaH₂ further compromises the grain structure inside the particles. Following 15 hours of ball milling, incorporating CaH₂ significantly accelerates the hydrolysis of aluminum, yielding hydrogen at a maximum efficiency of 97.8% [157]. Aluminum powder's water reaction may be efficiently accelerated by adding magnesium and lithium in high-temperature environments. Nevertheless, Bi, Zn, and S have minimal impact on the hydrolysis process of aluminum [158].

Nowadays, carbon materials have a great influence on aluminum hydrolysis activity. An Al-organofluoride (OF)-Bi alloy has been obtained by ball milling by Xiao et al., and it greatly enhances hydrogen production from tap water. At 50°C, the Al-7.5%Bi-2.5%OF alloy showed good hydrolysis capability, generating a highest of 5622 mL/min.gm [159]. As a milling-assisted agent, graphite and 2 wt.% NaCl may significantly enhance aluminum's reactivity in water. At temperatures lower than 45°C, the 76.5%Al/23%graphite composite material reacts with water to produce hydrogen in 6 h. Raising the reaction temperature results in a greater rate of hydrogen

production, peaking at 75°C [160]. Additionally, it has been found that composite materials made of activated aluminum, carbon, and thinner graphene nanosheets (GNS) can enhance the efficiency of water reactions. The composite material with the highest hydrogen production yield and rate was found to be Al-2.5 % GNS-7.5 % nanoBi [161]. Jia et al. have synthesized an Al/Ni composite utilizing Ni and Al, which, following hydrolysis, generated an Al/Ni micro-cell. The amount of hydrogen increases from 720 mL/g to 1170 mL/g due to the aluminum-water interaction [162]. Fe, Ni, and Co incorporate with Al to produce a galvanic reaction that diminishes corrosion potential and enhances current [163]. This has been further verified by Wang et al [164]. TiO_2 , $\alpha\text{-Al}_2\text{O}_3$, and $\gamma\text{-Al}_2\text{O}_3$ can be utilized to alter the surface of Al particles. Because of its fast induction time and low nucleation energy barrier, $\gamma\text{-Al}_2\text{O}_3$ modified Al powder has a much greater hydrogen production rate than $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 [115].

A conventional melting alloying method has prepared alloys using a smelting furnace. **Figure 2.1** illustrates the alloy synthesis procedure. Meng et al have also experimented with Al-Ga-Sn-In, Al-In-Sn, and Al-Ga with various ratios of these elements. They confirmed that the Al-Sn-In and Al-Ga alloys did not react with water below 65°C, and the Al-Ga-Sn-In alloy exhibited its best result when the weight ratio of In to Sn was 3:1, with a Ga content of 3% [165]. Moreover, liquid metal embrittlement (LME) occurs due to the wetting of surfaces and intergranular infiltration of eutectic Ga-In-Sn (GIS) into polycrystalline aluminum, resulting in a loss of ductility in the absence of applied stress. The Al-x wt.-%-GIS (x=5, 10, and 20) composites exhibit similar distinctive hydrolysis [166]. On the other hand, BiLi_3 formation during ball milling is responsible for the excellent water reaction performance of Al-Li-Bi alloy [117]. Manilevich et al. have illustrated the hydrogen production behavior of the composites of aluminum prepared by the melting method and eutectic Ga-In-Sn with the addition of bismuth (Bi) and antimony (Sb). They have found that

the alloy Al-Ga-In-Sn demonstrates the most effective stimulation of the hydrolysis process. Although Bi and Sb have close standard electrode potentials, incorporating bismuth into the Al-Ga-In-Sn alloy greatly lowers hydrolysis. In contrast, including antimony has little effect on the process [167]. Wu et al. have investigated three different composites of Al, Ga, In, Sn, and Bi and found that the Al-Ga-In₄Sn-InBi quinary alloy and the Al-Ga-In₃Sn quaternary alloy have provided vigorous hydrogen generation than Al-Ga-In₄Sn. However, the Al-Ga-In₄Sn-InBi quinary alloy has supplied hydrogen at a stable rate [154]. The experiment conducted by Meng et al. (**Figure 2.1**) shows that the Al-11%Ga-3%In-1%Sn alloy has excellent hydrogen generation performance, reaching a hydrogen conversion rate of 98%. According to this study, the optimal In/Sn ratio in the Al-Ga-In-Sn quaternary alloy limits the impact of Ga presence on hydrogen generation by hydrolysis and encourages the aluminum-water interaction. This implies that by encouraging the aluminum-water interaction, lowering the Ga concentration can reduce hydrogen production costs [168].

2.3.2.3 Mechanism of activated aluminum reaction with water

The reaction of activated aluminum with water takes place through different mechanisms. The micro-galvanic interaction between aluminum and the additive constitutes the chemical catalytic mechanism, whilst adding additives to the composite material promotes the physical catalytic mechanism. This process releases these additives from the surfaces or interiors of the particles, creating space for more active sites. The active aluminum composite transforms its microstructure and reaction area, enabling the reaction through this process. These two mechanisms are discussed in this section in detail.

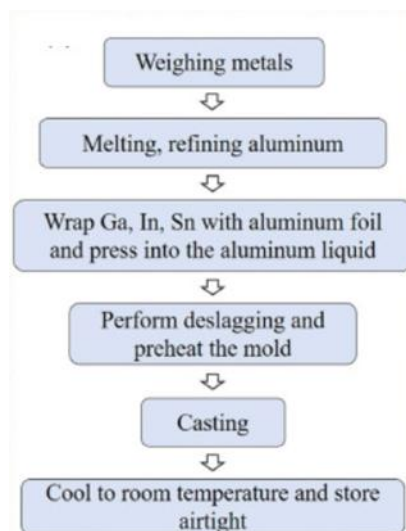


Figure 2.1: Alloy synthesis process of Al with Ga, In, Sn [168].

2.3.2.3.1. Chemical catalytic mechanism

Adding low melting point metals like In, Bi, and Sn to aluminum induces a micro-galvanic reaction during the reaction process. These metals possess higher standard electrode potentials than aluminum powder, creating numerous microgalvanic cells that facilitate galvanic reactions [157,169–171]. When SnCl_2 and aluminum are milled together, a solid-state reaction occurs on the metal surface, producing highly reactive Sn particles and aluminum chloride (AlCl_3) crystals. The Sn particles then interact with aluminum to form micro-galvanic cells, initiating the aluminum–water reaction for hydrogen generation. However, including Bi lowers the OH group (from water) adsorption energy on the outer surface of Al [172]. Fan et al. developed an Al-Li-Bi alloy using ball milling, consisting of three alloy phases: Al, BiLi_3 , and Al-Li. Due to the standard electrode potential of these alloys surpassing the requisite water decomposition potential, these alloys react with water. The first hydrolysis reaction center in the Al matrix is BiLi_3 , yielding Bi, LiOH, and H_2 . Al and the Bi combine to create a micro galvanic cell, which corrodes Al when catalyzed by an alkaline solution [117]. Minimizing the distance between the activation metals and aluminum enhances aluminum's galvanic corrosion. This happens consistently among the

aluminum particles, subsequent in many micro-galvanic contacts between the cathodic element and the anodic aluminum throughout the hydrolysis reaction. Davies et al. demonstrated that incorporating more than 1 wt% nickel (Ni) with bismuth (Bi) achieved complete activation of aluminum, rendering these composites non-reactive [173]. A reaction mechanism was proposed by Guan et al. for the Al-Ga-Sn-In quaternary alloy. It includes the interaction of an aluminum alloy with a granular or layered structure with water, leading to heat release. A eutectic reaction occurs due to the processing temperature significantly above the melting point of InSn_4 , allowing Al atoms to seep into this melted phase. Ga has a catalytic action comparable to InSn_4 because of its same eutectic temperature of 26.6°C [174]. The liquid metals Ga and Hg may electrochemically corrode aluminum particles to produce hydrogen, and they can also directly erode alumina on aluminum particles to make alloys [113]. The hydrolysis process of LiH catalyzes aluminum corrosion by generating OH^- ions, which in turn leads to the formation of LiOH. This LiOH compound can then facilitate both surface alumina and interior aluminum corrosion. Lithium hydroxide (LiOH) may also react with aluminum hydroxide ($\text{Al}(\text{OH})_3$) to produce lithium aluminate ($\text{LiAl}_2(\text{OH})_7 \cdot x\text{H}_2\text{O}$), which enhances the rate of aluminum's interaction with water. The catalytic process is analogous to activated aluminum composites containing CaH_2 [157,175]. Temperature-dependent changes in corrosion current density and the corrosion potential of aluminum were observed in the research of the induction of Fe, Co, and Ni in Al. The findings demonstrated that a rise in reaction temperature was associated with a drop in corrosion voltage and a boost in corrosion current, which raised the speed of the water reaction [163].

2.3.2.3.2. Physical catalytic mechanisms

By the gas atomization method, Liu et al. made two composites, Al-20Sn and Al-20Bi. The difference in linear thermal expansion coefficients between Al and Bi in Al-20Bi, coupled with

the exothermic characteristics of the hydrolysis reaction, results in the easy detachment of Bi-rich regions on the powder surface upon contact with water, consequently revealing fresh Al grain surfaces that trigger the hydrolysis reaction. The Al crystal grains are destroyed, and particle rupture begins with the growth of hydrogen bubbles. On the other hand, Sn is difficult to escape because it is uniformly distributed along the Al grain boundaries. Gradually passivating the Al-20Sn composite surface allows for a delayed onset of the hydrolysis process. Water will progressively seep into the powder during hydrolysis from the grain boundary openings, resulting in the powder eventually forming petals after a lengthy reaction [140]. Ga, In, and Sn deteriorate aluminum oxide layers by making Ga-In₃Sn eutectic compounds, causing cracks and dents, and, as a result, aluminum alloys allow easy hydrolysis. Moreover, aluminum may be entirely dissipated in Ga-In₃Sn eutectic compounds, inhibiting oxidation and acting as the activation site in the hydrolysis reaction [165]. Jin et al. investigated the role of Sn and In in Al-Ga-based alloys to better understand the insight of hydrogen production. They revealed that higher In-containing liquid metal alloys made broader and longer cracks than Sn-containing or lower In-containing alloys [176]. Lynch demonstrated that the lower melting point of indium (In) compared to tin (Sn) accelerated the propagation of fractures in the aluminum (Al) matrix, because In transitioned to a liquid state at the reaction temperature and facilitated its penetration into the Al matrix [177]. Additionally, Ga-Sn and Ga-In eutectics were also studied by Jin et al. They discovered that the gallium content in the Sn-containing sample's grain boundary phase (GB) always surpasses that of the In-containing sample. In contrast, the gallium concentration within the grains of the Sn-containing sample decreases noticeably. Specifically, tin (Sn) reduces the solid solubility of Ga in Al more than In does, indicating that Sn promotes the migration of Ga into the grain boundary (GB) phase more effectively than In. The solid solution of Ga would increase the cracking of the

Al matrix in In-containing materials, and Al matrix embrittlement would increase. Hence, a higher hydrogen yield would be achieved [176]. Moreover, He et al. worked with some alloys of Al-Ga-Sn-In with various ratios of alloying elements. They illustrated that below 40°C, the reaction did not last more than a few minutes. Furthermore, the amount of Sn in the composite influenced the hydrogen evolution rate. A concentration of 0.5 wt.% Sn resulted in the highest reaction rate, attributed to the formation of Ga-In-Sn (GIS) phases with fine granular and rod-like particle structures. Further rise in Sn content leads to the formation of sheet-shaped particles in GIS phases, which might impede the H₂ generation [178]. The Al/graphite composite's hydrolysis reaction entails water passing through the graphite layer, entering the Al/graphite interface layer, and generating hydrogen. The heat developed accelerates the hydrolysis process of aluminum and increases aluminum exposure by encouraging the breaking of the graphite layer [160]. Graphite accelerates the hydrolysis reaction of Al-30wt%Bi-10wt%C by fracturing the alloy and exposing additional corrosion sites in Al/Bi micro galvanic cells [138]. Xiao et al. combined aluminum with organic fluoride (OF) to create an Al-OF-Bi composite. During hydrolysis, water can enter the particles through the channels created by this multilayer structure. Aluminum's hydrogen generation rate increases as water molecules penetrate its particles, forming numerous microgalvanic cells between Al and Bi [159]. Salts like KCl and NaCl can be added to ball-milled particles to reduce their size and enhance their specific surface area. This results in active aluminum composite particles. This produces active aluminum composite particles. During water interactions, these salts reveal intracellular aluminum, enhancing the quantity of active sites. Chloride ions degrade the Al (OH)₃ generated by pitting corrosion [157]. Because of the dissolving heat of magnesium hydroxide and magnesium chloride, Fan et al. discovered that Al-Bi-salt or Al-

Bi-hydride mixes outperform Al-Bi alloys. Additionally, salt produces conductive ions that aid in developing microgalvanic cells made of Al-Bi alloy [153].

When aluminum interacts with water, it undergoes hydrolysis via a galvanic reaction between aluminum and a low-melting-point metal. Aluminum undergoes oxidation to produce Al^{3+} , whereas the H^+ ions from water undergo reduction to become hydrogen. However, the physical catalysis of the active aluminum composite changes its external and internal shape, which impacts the water reaction rate. This dual-mode catalysis, which is both chemical and physical, significantly speeds up the aluminum hydrolysis reaction rate.

Chapter 3: Methodology

3.1 Synthesis of Liquid Metal-Aluminum Composite

The eutectic liquid metal alloys are prepared using gallium (99.99%, Indium corporation), indium (99.99%, Fischer Scientific), and tin (99.99%, Fischer Scientific). The composition of the eutectic gallium-tin alloy (EGaSn) is 87.6% Ga and 12.4% Sn by mass (Melting point=20.5 °C) [179] and that of gallium-indium-tin alloy (EGaSnIn) is 68.5% Ga, 21.5% In, and 10% Sn by mass (Melting point=10.7 °C) [180]. Masses with the desired ratios are weighed and put in a ceramic crucible, heated using a heat gun, and mixed manually until the metals form a homogenous phase.

The steps of liquid metal-aluminum composites are summarized in **Figure 3.1** (a) and (b). The liquid metal (LM) suspension is prepared by placing a definite mass of the liquid metal in a glass vial filled with 20 ml of isopropanol, then sonicated using a probe sonicator at 50% power for 30 minutes (model Q125, Qsonica, USA) where ultrasonic waves disperse the liquid metal into fine particles, forming a stable suspension in the solvent. A preheating step is needed for gallium to melt it down before performing the sonication, as its melting point is slightly higher than room temperature[181]. Aluminum sheets are cut into square pieces and weighed, then evenly coated with the suspension using an airbrush to ensure uniform coverage. The solvent is left to evaporate, the sheets are weighed, and the mass of liquid metal and the liquid metal to aluminum ratio are calculated. A blow torch is used to thermally sinter the liquid metal-coated aluminum sheets, transforming them into a black, brittle solid. This solid is then manually ground into a fine powder using a mortar and pestle, and the resulting powder is stored in airtight glass vials.

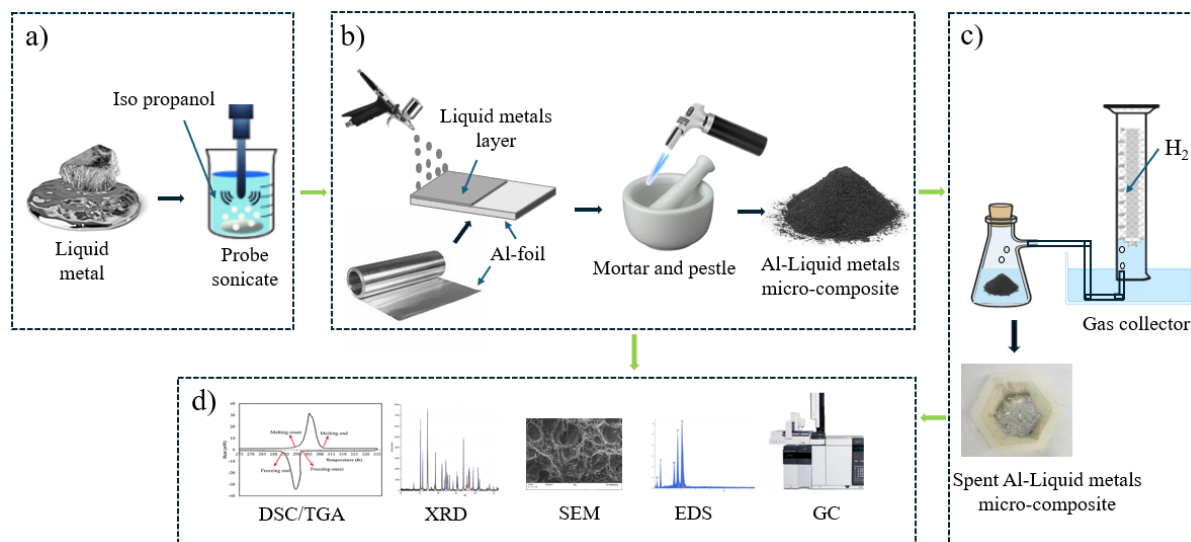


Figure 3.1: Experimental procedure for activated aluminum composite synthesis, hydrogen production reaction setup, and product analysis.

3.2 Hydrogen Production Reaction

One gram of the activated composite is placed in a conical flask with a side tube. 100 ml of distilled water is added to the flask and quickly sealed with a rubber stopper. The gaseous reaction products exit through a side tube connected with rubber tubing, allowing them to be collected.

The volume of generated gas is measured using the water displacement method demonstrated in **Figure 3.1** (c) where a graduated cylinder is filled with water and placed upside down in a water bath. The produced gas comes through the rubber tubing from the flask side tube, replaces the water in the cylinder, and the amount of collected gas is recorded. Dynamic data of the reaction were collected by recording the collected volume of hydrogen by taking time-lapse photos for the hydrogen collection cylinder at constant time intervals and analyzing them after the reaction fully stops.

Once the reaction is complete, a light grey powder forms. This powder is then collected and filtered using filter paper. The powder is dried on a hot plate, collected and stored for analysis.

3.3 Sample Analysis

XRD analysis was done for three samples with different mass ratios of liquid metal to aluminum for every composite (Ga-Al, EGaSn-Al, EGaSnIn-Al), before and after the reaction with water. A powder XRD pattern of the newly prepared and dried precipitate was obtained with a Rigaku Mini Flex II powder X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) in the range of 5 to 85 degrees with a rate of 5 degrees/min.

A field emission scanning electron microscope (FE-SEM) on a Quattro Dual Beam microscope at a 10 kV acceleration voltage was utilized for imaging samples of freshly prepared composite powders and powders produced after the reaction. The elemental mapping was analyzed using the EDS analyzer in the same equipment.

The composition of the reaction-produced gas was analyzed by gas chromatography (Agilent 7890a gas chromatograph) using helium as a carrier gas. The reaction was performed as described earlier, and the side tube from the flask was connected to a gas sampling bag to collect all the product gases. The collected gas was then manually injected into the gas chromatograph (GC) by squeezing the connected feed tube, allowing it to enter the GC column for analysis.

Differential Scanning Calorimetry (DSC) (TA instrument, Discovery DSC 250) was conducted to inspect the phase transformations of the synthesized samples. Approximately 6 mg of each sample was placed in a standard aluminum crucible and sealed, with an empty crucible used as the reference. The measurements were conducted under a constant nitrogen atmosphere to prevent oxidation, with a heating rate of 10 °C/min over a temperature range of 0 °C to 350 °C. The DSC thermograms were analyzed to identify endothermic and exothermic events corresponding to phase

transitions. The onset, peak, and end set temperatures were recorded to determine the thermal stability and characteristic phase transitions of the materials.

Thermogravimetric analysis (TGA) (Mettler Toledo - TGA/DSC2 thermal analysis star system) was also performed for the same samples at the same heating rate used in DSC, recording the mass change as a function of temperature, allowing the identification of mass changes related to moisture evaporation, decomposition, and phase transformations.

Chapter 4: Results and Discussion

4.1 Factors affecting hydrogen production

A set of experiments was performed to study the effect of the LM to Al ratio on the volume of produced gas, hydrogen yield, and the speed of reaction. The reaction can be visually observed by the formation of gas bubbles when water is added to the activated aluminum composite, which allows monitoring the onset and the end of the reaction. An immediate reaction of EGaSn-Al and EGaSnIn-Al composites with water at room temperature was observed. On the contrary, no observable reaction took place between Ga-Al composites and water at room temperature, even after a few hours. The reaction of Al-Ga composites with water starts when the reaction temperature is raised to more than 60 °C. The reaction is found to be very slow at this temperature, however, continuous agitation helped in reducing the reaction time. Therefore, all reactions were performed on Ga-Al composites with water at 70 °C with continuous agitation, and the reactions of EGaSn-Al and EGaSnIn-Al composites with water at ambient temperature without agitation.

The aim was to investigate how the mass ratio of liquid metal (LM) to aluminum (Al) affects the volume of gas produced; therefore, the reaction was performed using composites synthesized with different mass ratios of LM to Al, and the volume of produced gas for each ratio. The results of the reactions performed using various mass ratios for the three composites are shown in **Figure 4.1**. Composites of Ga-Al with a mass ratio of 0.17 produced 960 ml of gas volume per gram of composite; the volume decreases as the mass ratio of Ga to Al increases. EGaSn-Al composites showed a different profile as the volume of produced gas is low for low EGaSn to Al ratios, and the volume rises with the increase in the mass ratio. The maximum volume of produced gas is 780 ml/g at a mass ratio of 0.45. Further increase in the EGaSn ratio leads to a reduction in the volume of produced gas. Lastly, aluminum activated with a very small amount of EGaSnIn (7% mass ratio)

produced gas with a volume of 1120 ml/g. This is the largest collected volume among all the tested samples for all ratios. The volume of produced gas decreases with the increase in the EGaSnIn to Al ratio.

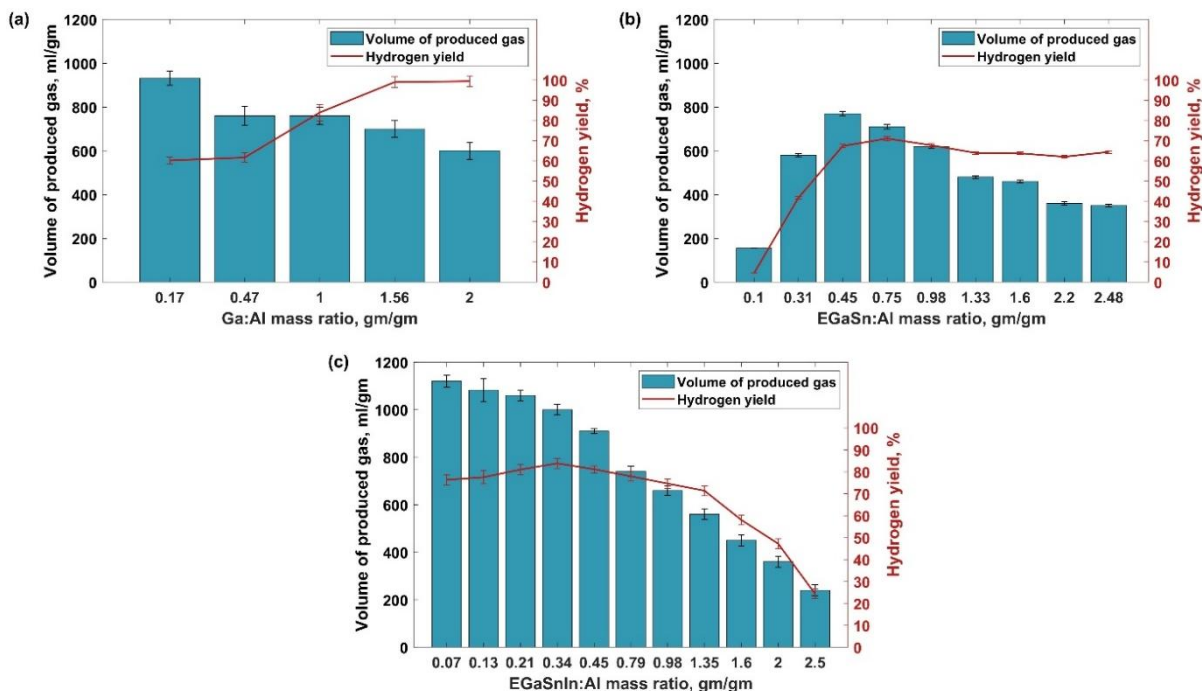


Figure 4.1: Volume of produced gas and hydrogen yield for three different composites with various ratios. a) Ga-Al at 70 °C (with agitation), b) EGaSn-Al at room temperature (without agitation), c) EGaSnIn-Al at room temperature (without agitation).

I sought to quantitatively investigate the efficiency of the reactions by analyzing the actual amount of hydrogen present in the collected gas samples using GC and calculating the hydrogen yield. Hydrogen yield is defined as the ratio of the actual amount of hydrogen produced to the theoretical maximum amount that would be generated if all the aluminum were fully consumed in the water-splitting reaction. It is a useful metric for comparing the performance of different activated composites that provides a quantitative measure of aluminum activation efficiency.

I analyzed gas samples collected from the reaction products of composites of the three liquid metals with different mass ratios of LM:Al. The analysis of all the samples showed the percentage

of hydrogen with mole ratios ranging from 63.6% to 87.1%. The rest of the gases are mainly nitrogen, oxygen, and carbon dioxide, with relative ratios that are very comparable to the typical ratios in air. This suggests that the reaction produced only hydrogen and that the other gases represent the air that was originally present in the gas production setup (the empty space in the reaction flask and the tubing) before the reaction started. Using the GC results and the volume of the collected gas, we calculated the volume of air present in all the tested samples. The calculations showed very comparable volumes of air in all the tested samples, with an average value of 144.8 ± 11.3 ml. Given this value, we calculated the volume of hydrogen in all the samples by subtracting the air volume from the total collected gas volume and the hydrogen yield for each sample using equations (11) and (12) based on the stoichiometry of reactions (9) and (10) and assuming that all the available aluminum in the composites reacts with water, producing only hydrogen.

$$n_{H_2, theoretical} = \frac{3 \times \text{mass of composite}}{2 \times 26.982 \text{ g/mol}} \times \frac{1}{1 + \text{mass ratio of LM to Al}} \quad (11)$$

Thus, the hydrogen yield is calculated as follows:

$$\%Yield = \frac{n_{H_2, measured}}{n_{H_2, theoretical}} \times 100\% \quad (12)$$

The calculated yields of all tested samples are shown in **Figure 4.1**. For Ga-Al composites, the hydrogen yield is ~60% for low gallium ratios, the yield increases with the increase in gallium mass ratio until it reaches around 100% at a gallium to aluminum ratio of 1.56 and higher. For the EGaSn-Al composites, the yield is very low for low EGaSn:Al mass ratios (<10%) and increases with the increase in the EGaSn mass ratio. The maximum yield is around 67% at a mass ratio of 0.75 and is almost the same for higher ratios. These results show that for low and intermediate LM mass ratios, the portion of aluminum activated by LM (and accordingly the hydrogen yield) is

proportional to the LM content in the composite. After a specific LM ratio, no more aluminum activation is achieved with the increase in the LM ratio. The reduction in the produced gas volume despite the high yield in cases of composites with high LM ratios is a result of the low aluminum content in these composites.

EGaSnIn-Al composites achieved a relatively high yield (76.3%), a very low LM mass ratio at very low EGaSnIn mass ratios. The yield increases slightly with the increase in the mass ratio and achieves the maximum yield of 83.8% at a mass ratio of 0.34. Contrary to the two previous composites, the yield decreases with further EGaSnIn ratio increases until it reaches ~25% at a mass ratio of 2.5. The initial increase in the yield with the increase of the EGaSnIn ratio is expected (as discussed in the previous two composites), however, further analysis was needed to explain the unexpected reduction in the yield with the increase in the EGaSnIn ratio. This will be discussed in detail in the analysis section.

The effect of the different liquid metals on the reaction speed and rate of gas production by collecting data on the volume of produced gas with time was also studied. The gas production volume and rate as a function of time are shown in **Figure 4.2**. As mentioned earlier, the reaction rate for Ga-Al composites with water is very slow despite performing the reaction at high temperature and continuous mixing. The reaction takes 20 hours until it fully stops for low Ga ratios; the time decreases to 10-12 hours for higher ratios. The reaction rate is consequently very low, the maximum recorded rate is less than 6 ml/gm.min and the average rate is ~2 ml/gm.min.

The reaction of activated EGaSn-Al composites is very fast. For all tested EGaSn to Al mass ratios (0.1 to 2.5), the reaction completely stops within 3.33 ± 2 minutes. More than 90% of the produced gas is generated within 1 minute for all the tested samples. The gas production rate in the beginning of reaction is very high and reaches 1200 ml/gm.min.

The EGaSnIn-Al composites reacted more slowly than the EGaSn-Al composites. The reaction of composites with a low EGaSnIn-Al mass ratio took ~18 minutes until the reaction fully stopped. The reaction time is the shortest at a mass ratio of 0.45; at this ratio, the reaction was completed after 6 minutes. The reaction time increased for composites having higher EGaSnIn to Al ratios. The gas production rate is high at the beginning of the reaction for all ratios; however, it is relatively low for low ratios and is the highest at a ratio of 0.45 (~270 ml/gm.min) and decreases with the increase in the mass ratio.

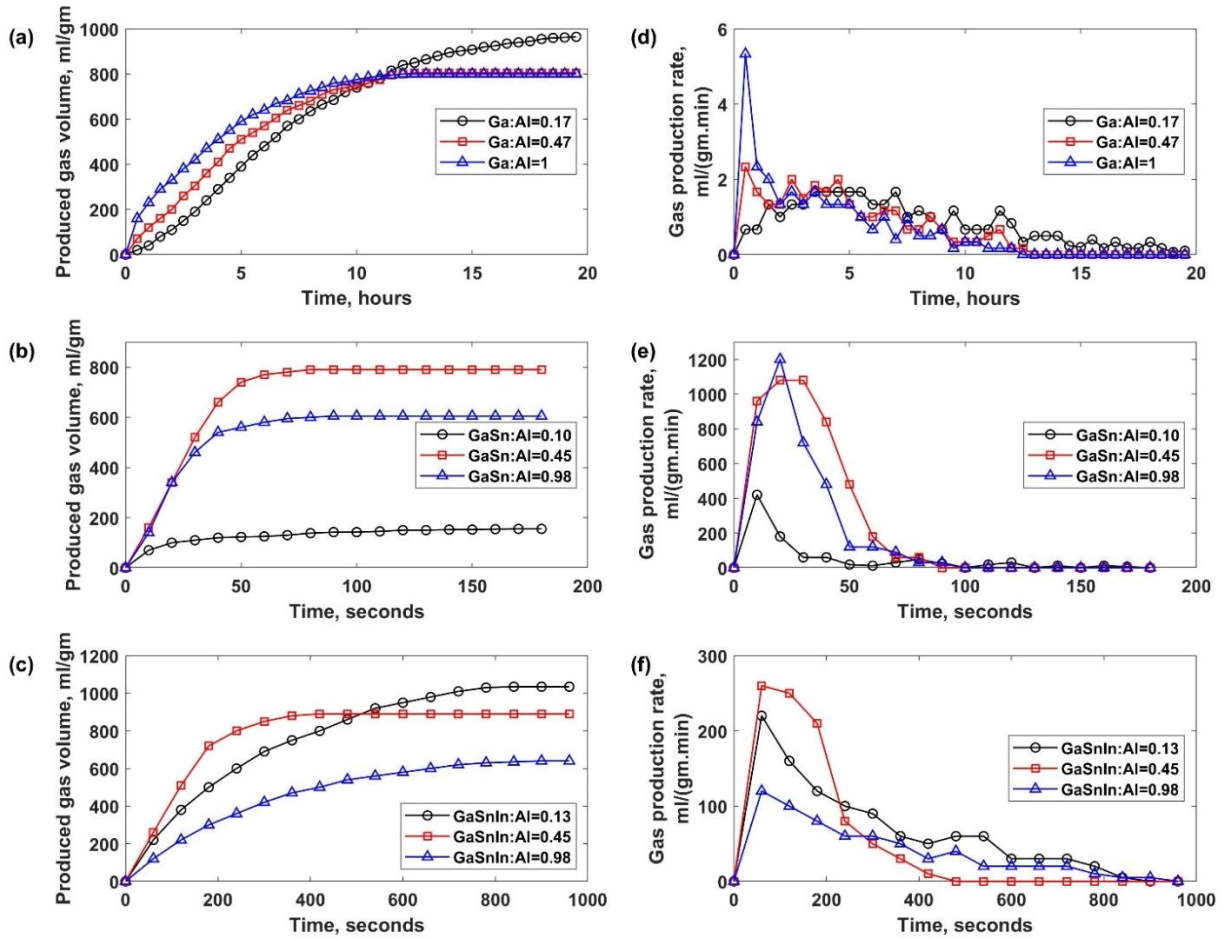


Figure 4.2: Cumulative produced gas volumes and rates of gas production as a function of time for (a) and (c) Ga-Al (70 °C), (b) and (d) EGaSn-Al (30 °C), (e) and (f) EGaSnIn-Al (30 °C).

These results, in addition to the results of our recent study of activating aluminum with eutectic gallium-indium liquid metal alloy (EGaIn) [182], clearly show the influence of tin and indium in

speeding up the reaction of thermally activated gallium-aluminum composites with water. The high rate of reaction of water with aluminum activated in presence of tin (EGaSn) and the large volume of gas produced from the reaction of water with aluminum activated in presence of In (EGaIn) agree with a previous study that showed that tin catalyzes and speeds up the water splitting reaction and indium increases the area of aluminum exposed to the reaction by inducing cracks in aluminum [176]. The volume of produced gas from the reaction of water with aluminum activated using EGaSnIn is slightly larger than that produced from aluminum activated using EGaIn. The combined effect of indium and tin in aluminum activation and the influence of the mass ratio of EGaSnIn to Al on the produced gas volume, hydrogen yield, and rate of reaction are discussed in the analysis section.

The influence of reaction temperature on reaction time was studied for thermally sintered EGaSn-Al and EGaSnIn-Al composites with different mass ratios. This did not include Ga-Al composites in this study since their reactions with water have already been performed at elevated temperatures. A hot plate or cold-water bath was used to control the reaction temperature with continuous temperature monitoring. The reaction time was recorded starting from the addition of water to the composite until bubble formation stopped. **Figure 4.3** summarizes the results showing a significant dependence of the reaction time on temperature. For instance, increasing the temperature from 10°C to 20°C significantly reduced the reaction time from 12.5 minutes to 4.75 minutes for EGaSn-Al composites and from 66 minutes to 18.5 minutes for EGaSnIn-Al composites. A further increase in temperature led to a further reduction in reaction time. For EGaSn composites, the reaction stops at 45 °C after less than 30 seconds, and stops after slightly less time with the increase in temperature. The minimum reaction time recorded for EGaSnIn composites is 1 minute at 70 °C.

Despite these variations in reaction time, the total volume of hydrogen produced remained consistent at all tested temperatures and composite ratios.

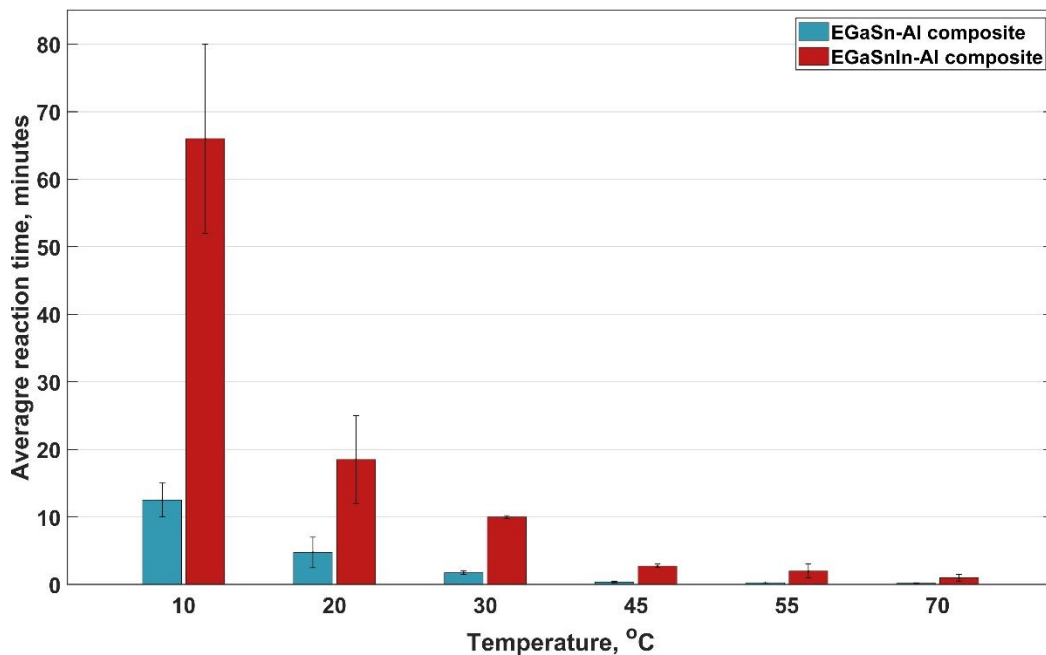


Figure 4.3: Reaction times of EGaSn-Al and EGaSnIn-Al composites with water at different temperatures.

The change of composite reaction activity due to storage was also investigated by preparing a large sample of EGaSn-Al and EGaSnAl composites with the ratio producing maximum volume of gas for each. The composites were stored in airtight glass vials under ambient conditions, and a sample of each composite was taken at different time intervals: immediately after preparation, 1, 3, 7, 15, 30, 60, and 90 days after preparation. **Figure 4.4** summarizes the experimental results where the generated gas volumes are normalized and expressed as a percentage of each composite's maximum volume of produced gas. The maximum volume corresponds to the volume produced from the reaction of the sintered composite immediately after preparation. The results show that the activated composites preserve more than 90% of their initial activity after two weeks of storage. The activity declines slowly with time and reaches slightly above 70% for EGaSn-Al composites and approximately 81% for EGaSnIn-Al composites. After three months, EGaSn-Al and EGaSnIn-

Al composites maintain 67% and 75% of their initial activities, respectively. It is anticipated that the composites will show higher activity for longer durations if stored in water vapor-free environments. Exposure to moisture is likely a major factor contributing to deactivation, which has been experimentally confirmed in other activated aluminum composites [183].

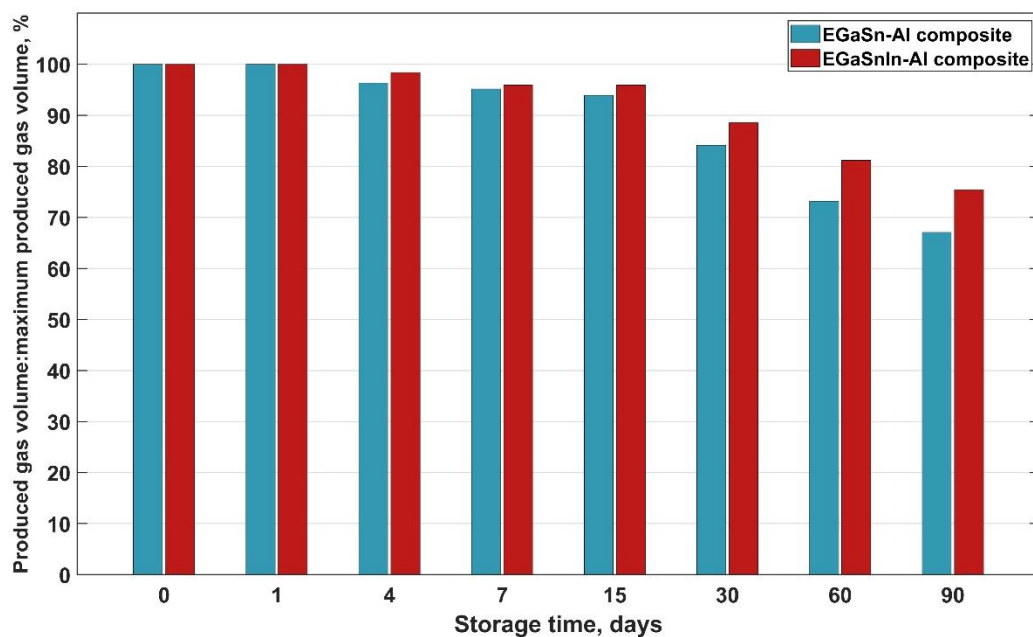


Figure 4.4: Effect of storage time on volume of produced gas.

4.2 Analysis and Characterization

Three samples of each composite (Ga-Al, EGaSn-Al, and EGaSnIn-Al) were analyzed with different liquid metal to aluminum ratios before and after reaction with water using XRD. **Figure 4.5** shows the XRD analysis results. The XRD patterns of the aluminum composites with the three liquid metals before reaction with water mostly show Al peaks. Nonetheless, small peaks of Ga and Ga₂O₃ are noticed for the Ga-Al composite with a high Ga ratio. Besides, small peaks of Sn are observed in EGaSn-Al and EGaSnIn composites. The XRD analysis shows very small or no peaks for Ga and the eutectic Ga alloys due to their low melting points, which are lower than the XRD operating temperature.

The XRD peaks of the products of the Ga-Al composites reaction with water (**Error! Reference source not found.**(b)) indicate the presence of AlOOH and Al(OH)₃ phases for all Ga:Al mass ratios, confirming that reactions (1) and (2) take place between activated aluminum and water. Residual peak of Al ($2\theta \approx 80^\circ$) is observed at low Ga: Al mass ratio, indicating that part of the aluminum is not activated and confirming that the increase in the ratio of gallium leads to activating a higher ratio of aluminum.

The peaks of unreacted Al are also observed in the reaction products of EGaSn-Al with water. The peaks are significantly large in the case of EGaSn-Al composites at low EGaSn: Al ratio, indicating the presence of a high ratio of unreacted aluminum. This agrees with the hydrogen yield results presented earlier. The aluminum peaks decrease with the increase in the EGaSn ratio, indicating more aluminum activation. Furthermore, Sn is identified in these samples, unlike **Figure 4.5** (c), where the predominant presence of highly crystalline Al may have concealed the Sn peaks. The existence of Al(OH)₃ and AlOOH phases confirms the creation of reaction products, however, the wide peaks reflect a lower level of crystallinity in comparison with Ga-Al composite peaks.

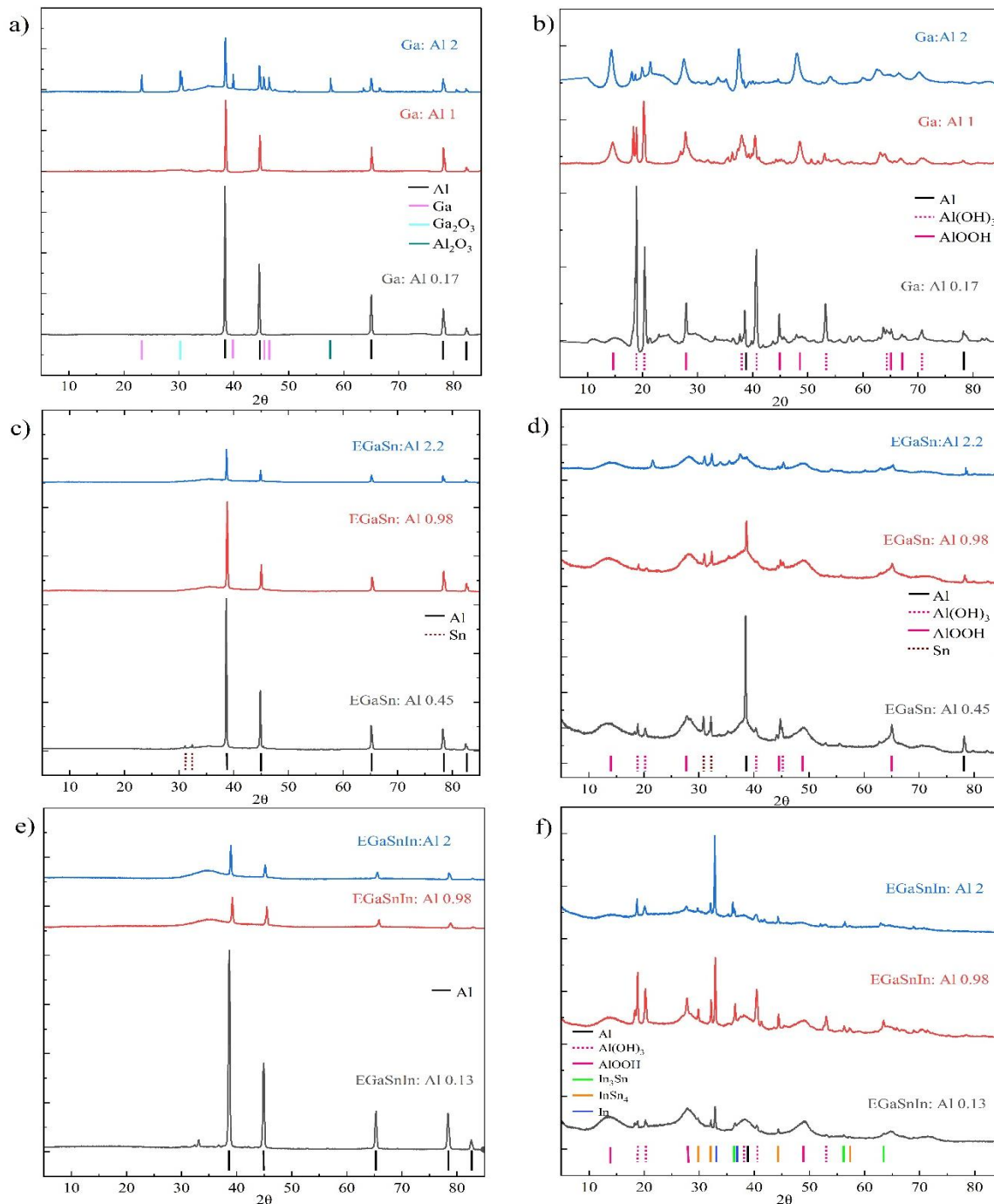


Figure 4.5: XRD plots for Ga-Al composites a) before reaction, b) after reaction; EGaSn-Al composites c) before reaction, d) after reaction; EGaSnIn-Al composites e) before reaction, f) after reaction.

The peaks of $\text{Al}(\text{OH})_3$ and AlOOH are observed in the XRD pattern of the EGaSnIn composite reaction product, which suggests the same aluminum reactions with water as in the previous two

composites. Besides, peaks of In and Sn intermetallic compounds (In_3Sn and InSn_4) are also observed. The height of the peaks increases with the increase in the EGaSnIn ratio, indicating more intermetallic formation at high ratios, especially for the InSn_4 phase ($2\theta=32^\circ$). Moreover, the In phase ($2\theta=32.8^\circ$) also becomes prominent in a higher ratio.

We analyzed the reaction products of EGaSnIn-Al composites with three different EGaSnIn:Al ratios using TGA and DSC to get a better understanding of the In-Sn intermetallic alloys formation during the reaction. TGA analysis results in the temperature range 0-500 °C (supplementary materials, figure A4) showed typical solid drying curves for the three samples indicating no excessive oxidation, thermal decomposition or other phenomena within the test temperature range. **Figure 4.6** shows the DSC analysis results of the three samples within a temperature range of 0 to 350 °C. For low EGaSnIn:Al ratio, the endothermic peak observed at 115°C corresponds to InSn_4 phase. A small endothermic peak (or shoulder) at ~156 °C appears for reaction products of composites having intermediate EGaInSn ratios, this peak becomes more pronounced at higher EGaSnIn ratios. This peak temperature corresponds to the bulk melting temperature of pure indium and indicates a high extent of indium formation at high EGaSnIn ratios, which agrees with the XRD results. No peaks of In_3Sn were observed in the tested samples, we attribute this to the melting temperature of In_3Sn (135 °C) which is intermediate between those of InSn_4 and indium. We anticipate that a small peak of In_3Sn is present (which corresponds to a small amount of In_3Sn), but is not observable due to the presence of two big peaks before and after this peak. The combined results of XRD and DSC analyses show that In_3Sn is formed in a small quantity compared to InSn_4 . The formation of indium-tin intermetallic compounds and the presence of free indium explain the reduced hydrogen yield at high EGaSnIn ratios, as a fraction of both indium and tin is consumed

in the intermetallic formation without contributing to aluminum activation. This effect is more observable in the composites having high EGaSnIn ratios as shown earlier.

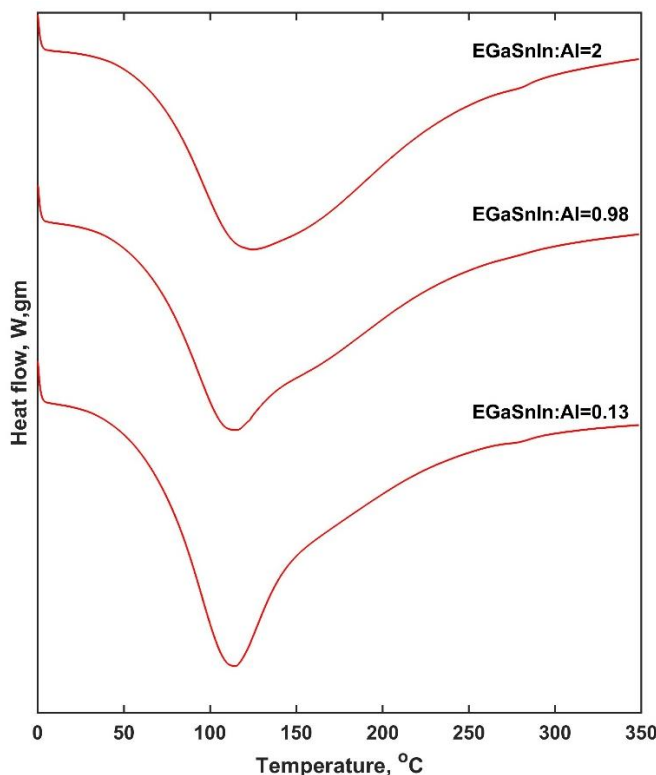


Figure 4.6: DSC results of reaction products of EGaSnIn-Al composites having different EGaSnIn:Al mass ratios

I examined the structure of the composites before and after reacting with water using a scanning electron microscope. **Figure 4.7** shows the imaging results of one sample of each composite. We imaged samples with LM: Al ratios that produce the maximum gas volume. The images show that for the three composites, the products contain a lot of fine particles whose size is significantly smaller than that of the composites before reacting with water. This is a result of the reaction of aluminum with water and the formation of aluminum hydroxides. Nevertheless, there are also relatively larger-sized particles in the reaction products of the three composites. We anticipate that these are particles of unreacted aluminum, as we have previously shown that the composites with

the LM: Al ratios used do not achieve very high hydrogen yield (which means that not all aluminum reacts with water).

The comparison of **Figure 4.7** b, d, and f indicate that the reaction products' average particle size in the case of EGaSnIn-Al composites is smaller than that of Ga-Al and EGaSn-Al composites. The reduction in particle size can be attributed to the presence of indium that forms deep cracks in the aluminum matrix, leading to its fragmentation and exposing a larger number of aluminum molecules to the reaction. We previously observed a similar size of reaction product particles using thermally sintered EGaIn-Al composites [182], which confirms that the presence of indium is the main cause of the reduced particle size of reaction products and explains the high hydrogen yield that is achieved in the presence of indium. A similar trend is observed in SEM images of other samples synthesized using different LM:Al ratios (Supplementary materials, figures A1 and A2).

4.3 Proposed Mechanism

Based on the experimental results and analyses performed, we built a good understanding of the role of each element in activating aluminum and in hydrogen production rate and quantity. We suggest the following mechanism of reaction based on our observations and on published reaction mechanisms of other activated aluminum composites.

We anticipate that aluminum activation by gallium is a result of the different standard electrode potentials of Ga (-0.56 V) and aluminum (-1.662 V) which promote micro-galvanic reactions leading to hydrogen production. This mechanism is proven for other aluminum composites activated using elements having standard electrode potentials higher than that of aluminum [169,184,185]. The EDS mapping of reaction products (supplementary materials, figure S3) shows even distribution of gallium and aluminum over the scanned area and supports this hypothesis.

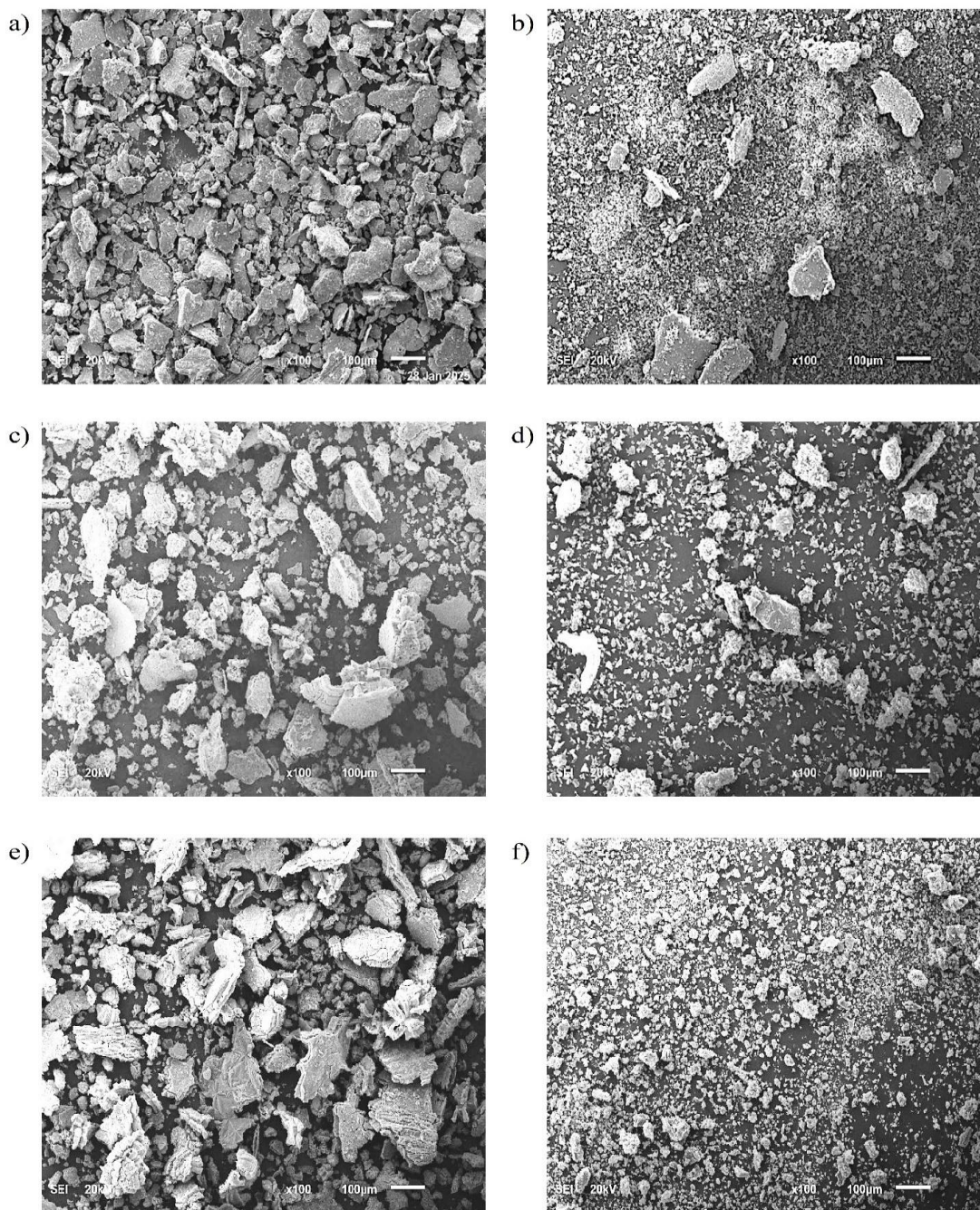


Figure 4.7: SEM images of Ga-Al composite with mass ratio 0.17 a) before reaction, b) after reaction; EGaSn-Al composite with mass ratio 0.45 c) before reaction, d) after reaction; EGaSnIn-Al composite with mass ratio 0.13 e) before reaction, f) after reaction.

The enhanced rate of reaction in the presence of tin and high produced hydrogen volume in the presence of indium that we reported agree with the results reported with aluminum activation in the presence of the same elements by ball milling [176] and suggest a similar mechanism in the

case of thermal sintering. We speculate that low-melting-point phases of In and Sn with Ga form at the grain boundaries (GBs) of Al–Ga composites, which create diffusion channels enhancing the contact between water and Al. The In-containing phase has a low melting point and intrinsic brittleness, causing wide and deep cracks in the aluminum matrix, leading to excessive aluminum pulverization in water and increasing the number of aluminum atoms exposed to reaction. The low melting point phase in the case of Sn does not form deep cracks as in the case of In, however, it increases the rate of gallium penetration to the grain boundaries and hence speeds up the micro-galvanic reaction with aluminum and the rate of hydrogen production.

Activating aluminum using EGaSnIn leads to combining the influences of In and Sn on the reaction by enhancing both the reaction rate and the hydrogen yield using a very low ratio of EGaSnIn. The formation of In-Sn intermetallic compounds in the case of high EGaSnIn:Al ratios is expected to be a result of the presence of In and Sn in high ratios and the formation of local hot spots due to the exothermic nature of the aluminum hydrolysis reaction.

Chapter 5: Conclusion

The activation of aluminum was studied by thermal sintering using low melting point metal Ga, and eutectic gallium alloys EGaSn and EGaSnIn as activating agents. Activating aluminum offers a promising route to hydrogen production as it reacts spontaneously with water to produce hydrogen through a water splitting reaction.

My experiments showed that the three liquid metals can be used for aluminum activation, however, the reaction speed and hydrogen yield were found to be different from one metal to another. Ga-Al composites containing a low Ga ratio react with water at 70 °C with continuous agitation, producing hydrogen with a yield of ~60% in ~20 hours. Composites having higher ratios of Ga achieve a yield up to 99.4%, however, the reaction time is still long. Addition of Sn to Ga leads to a significant reaction acceleration, as the reaction takes 3.33 ± 2 minutes for all ratios of EGaSn used. However, the composites of Al with EGaSn achieved hydrogen yields of less than 70%. Composites of Al with EGaSnIn achieved decent hydrogen yield using an EGaSnIn: Al mass ratio of only 7%. For all ratios of EGaSnIn used, the reaction takes 8-17 minutes until it fully stops.

My results showed that the reaction rate of Al-EGaSn and Al-EGaSnIn with water is highly dependent on the reaction temperature, which offers a simple and efficient way of controlling the reaction time. Furthermore, the composites proved to have a long shelf life as they retain ~70% of their reactivity after 3 months of storage at ambient conditions.

I think the reaction is a result of the formation of micro-galvanic cells on the micro scale between gallium and aluminum, which drive the water splitting reaction. We also speculate that tin catalyzes the reaction, leading to short reaction time, and that indium helps in creating cracks in the

aluminum matrix, leading to exposing a large amount of Al to the reaction, consequently increasing hydrogen yield.

In this thesis, I presented the results of composite reactions with distilled water. Our preliminary tests on hydrogen production from the reaction of composites with non-distilled water (like tap water and water with high salinity) are very promising and indicate the possibility of using composites to produce hydrogen directly from river or sea water, which is an interesting point for a future study.

The simple and quick composites synthesis process, besides the high hydrogen yield and high reaction speed of the composites, makes them very promising for on-demand production of hydrogen using water as a safe, abundant, easy-to-handle, and cheap hydrogen carrier.

Further investigations are required to get a deeper understanding of the activation mechanism of aluminum by thermal sintering and the mechanism of reaction between water and thermally sintered composites. Several challenges must be addressed for the larger-scale use of the composites in an economically feasible process, such as the management of product oxides and the recovery of the liquid metal from the reaction products.

Appendix

Figure A1 illustrates that the mass ratio for EGaSn to Al has no impact on the particle size for both freshly prepared and spent samples, which supports the experimental yield data. The yields for both samples are almost identical. On the other hand, the higher mass ratio of the EGaSnIn-Al composite produces smaller particles (**Figure A2**) after reaction, compared to the lower ratio, which depicts the higher yield that is also verified by the experimental data. There is almost a 5% rise in yield from the ratio of 0.13 to 0.98.

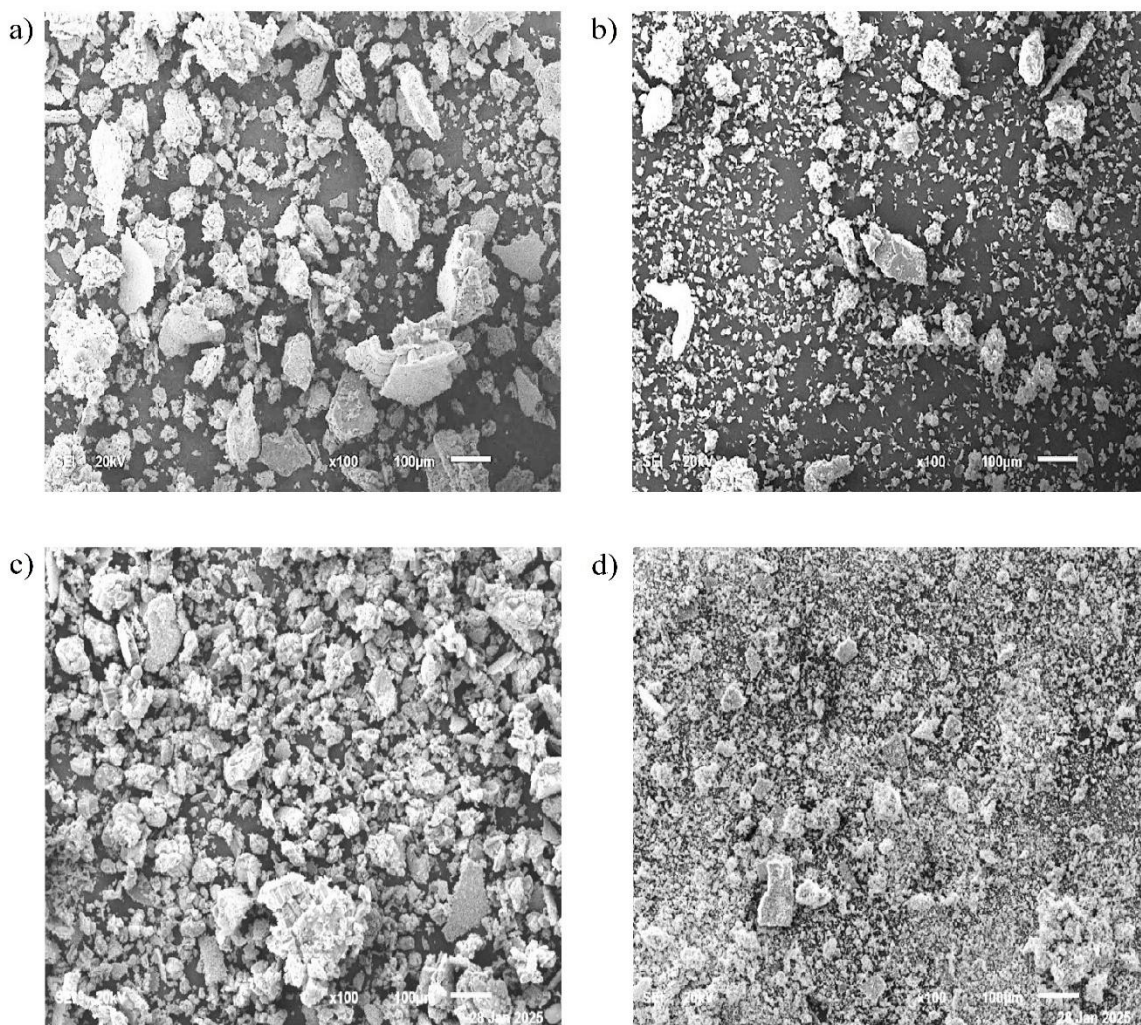


Figure A1: SEM images (100x) for EGaSn-Al composite with mass ratio 0.45 a) before reaction, b) after reaction; EGaSn-Al composite with mass ratio 0.98 c) before reaction, d) after reaction.

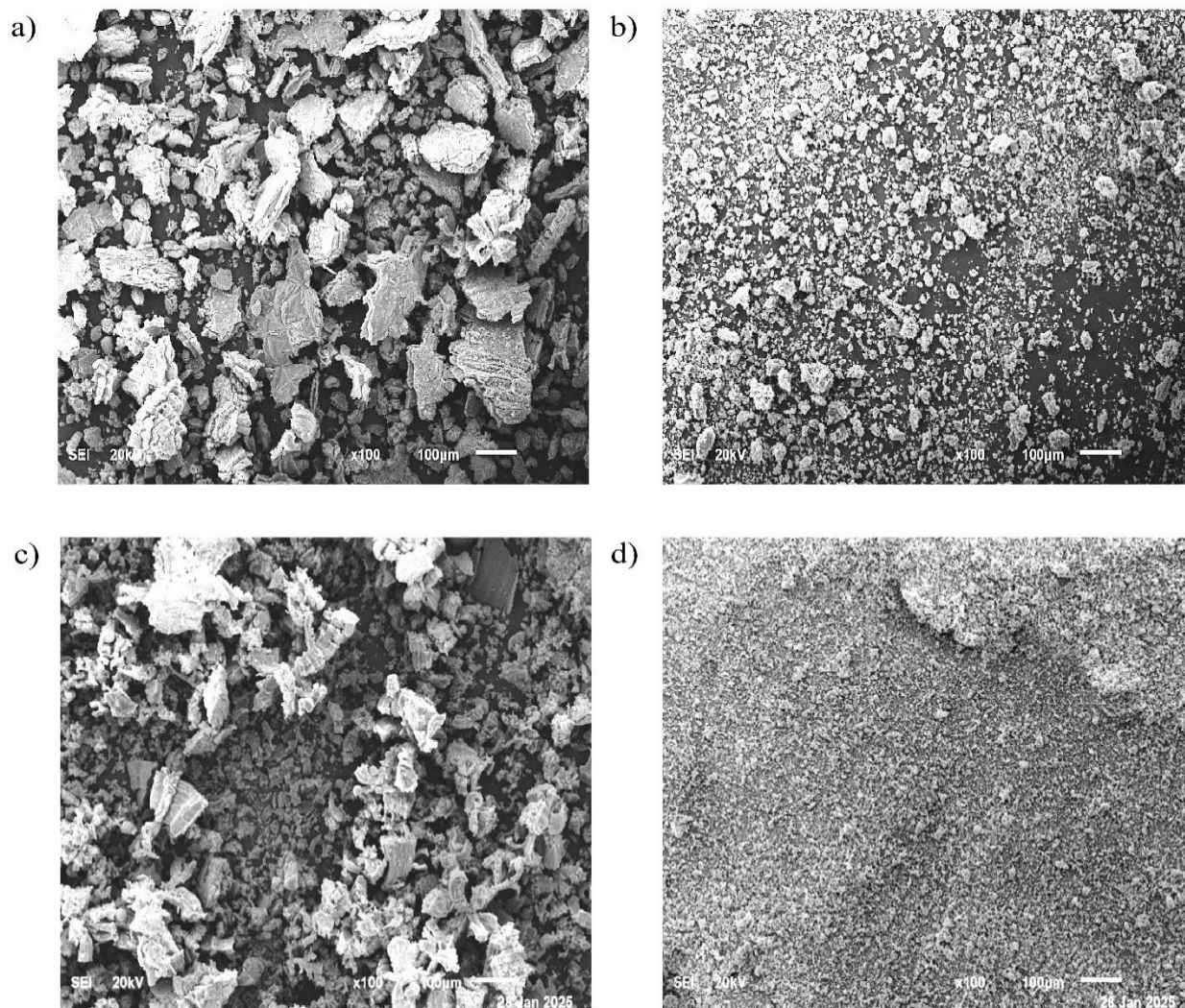


Figure A2: SEM image (100x) for EGaSnIn: Al composite with mass ratio 0.13 a) before reaction, b) after reaction; EGaSnIn: Al composite with mass ratio 0.98 c) before reaction, d) after reaction.

From **Figure A3**, it is seen that the sample of EGaSn-Al with the mass ratio of 0.45 contains a higher amount of Ga and Sn, and a lower amount of Al in comparison with the EGaSnIn-Al composite with the ratio of 0.13, which is obvious due to the higher ratio of liquid metals in the EGaSn-Al composite. However, though EGaSnIn-Al has higher Al content than EGaSn-Al

composite, the weight of oxygen is less, which also proves the higher activation of EGaSnIn-Al than the other one by reducing the oxide layer on Al.

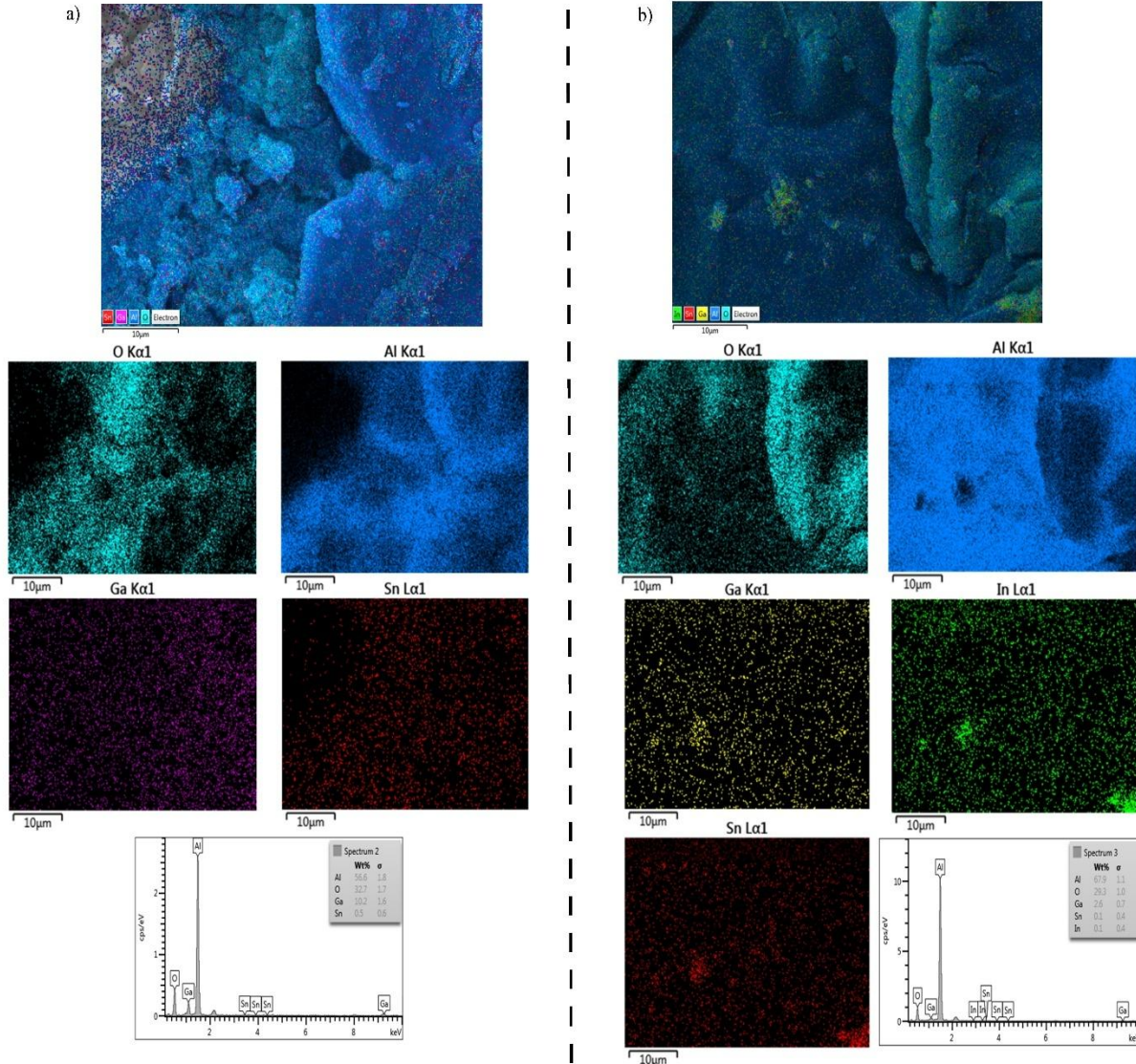


Figure A3: EDS analysis of freshly prepared sample of a) EGaSn: Al=0.45, b) EGaSnIn: Al=0.13

Figure A4 illustrates the TGA plots for three ratios of EGaSnIn to Al (0.13, 1, and 2), which were performed in the temperature range from 20 to 500°C. It is seen that all three ratios provided similar characteristics in TGA analysis. The mass of the samples was gradually reduced to ~200°C. The mass change rate curves show a sharp rate change to around 100°C. At a lower ratio, the peak

reduction rate was observed at around 81°C, and this temperature was raised with the ratio, reaching 112 to 124°C at a ratio of 2. However, this plot is similar to the plot of drying. The first portion of weight reduction was due to the surface/unbounded water reduction, which was faster, then the bounded water reduction happened, which was slower than the surface/unbounded water reduction. At a lower ratio, there might be a higher proportion of unbound water than bounded water, and the opposite might also be true for a high ratio of EGaSnIn to Al. Therefore, the peak reduction rate for a higher ratio was observed at higher temperatures.

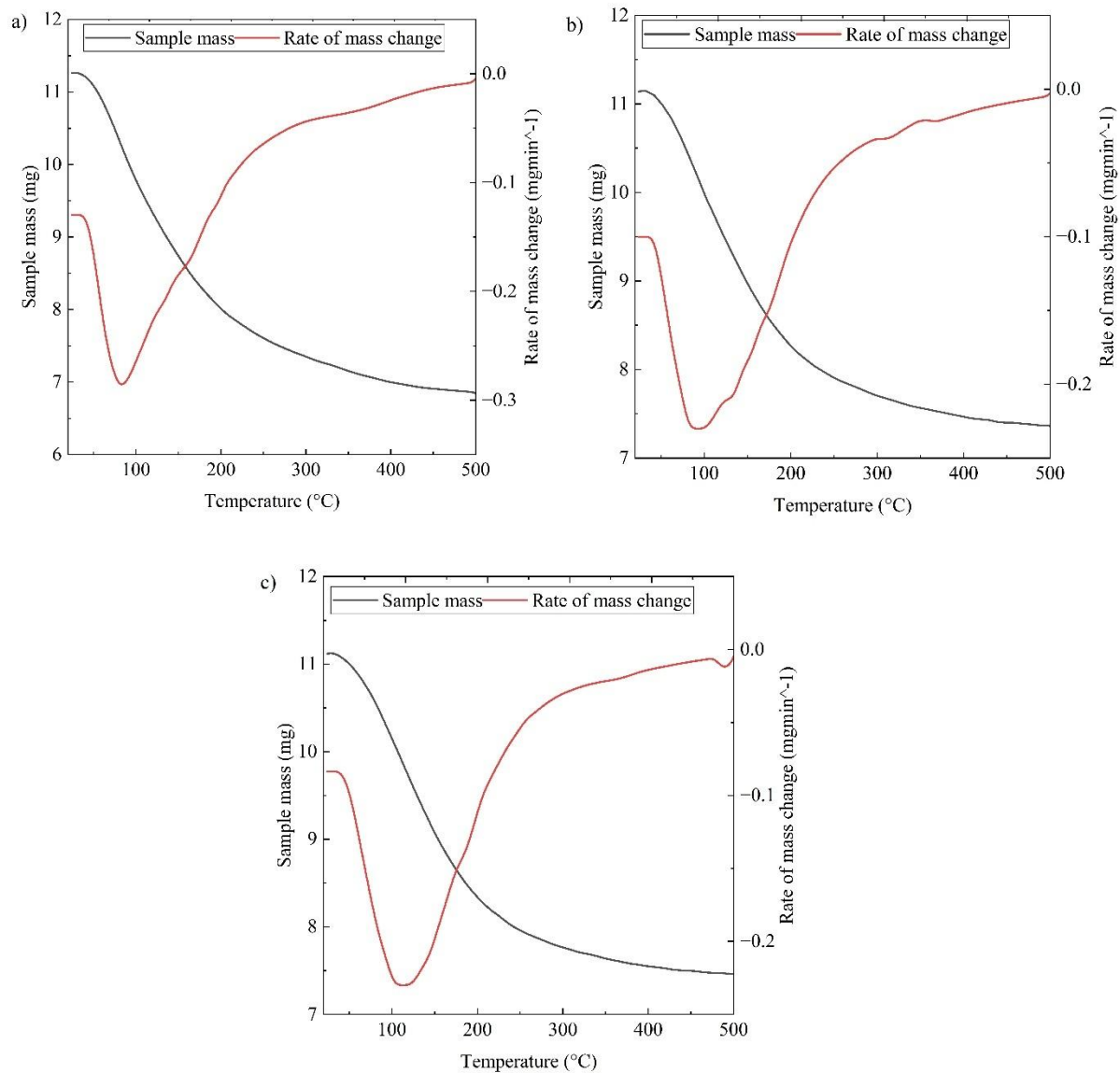


Figure A4: TGA for the spent composites of EGaSnIn- Al for the ratios of a) 0.13, b) 1, and c) 2.

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Vitae

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ACADEMIC BACKGROUND

- **King Fahd University of Petroleum and Minerals (KFUPM), KSA.**

MSc. in Chemical Engineering (2023-2025)

Credit: 30.

CGPA: 3.75/4.00

- **Shahjalal University of Science & Technology (SUST), Bangladesh.**

BSc. (Engg.) in Chemical Engineering & Polymer Science (2016-2021)

Credit: 165.

CGPA: 3.50/4.00.

EXPERIENCE

- Research Assistant (October 2023- Current) at Catalysis Research Lab, affiliated with the Interdisciplinary Research Center for Refining and Advanced Chemicals, KFUPM, KSA.
- Teaching Assistant (Fluid Mechanics, Elementary Principle of Chemical Process, Heat and Mass Transfer Lab, and Fluid Mechanics Lab) (January 2023- Current), Chemical Engineering, KFUPM, KSA.

- Voluntary research assistant (February 2021 to May 2022) at Bioenergy and Bioremediation Lab, SUST, Bangladesh.

RESEARCH PROJECTS

- Hydrogen generation through aluminum activation using liquid metal additives and recovery. (October 2023 to May 2025)
 - ✓ Examine the effect of various compositions and ratios, water source, temperatures, and shelf life of composites on Hydrogen yields. I am utilizing XRD with OriginPro to visualize peaks and X'pert HighScore Plus to analyze phases on composites, SEM and EDX with ImageJ software to visualize composites' morphology and particle size before and after reactions. DSC and TGA were also used to examine the phase change in composites with temperature change from 0 °C to 350 °C. Moreover, I am analyzing gas samples using GC.
- Utilizing rice straw as a raw material for pulp and paper production. (January 22- November 22)
 - ✓ Studying the effect of pulping methods and rice straw-to-liquor ratios on pulp yield, kappa number (using TAPPI Standard T236 cm-85), silica disposition on pulp, and produced paper quality, such as the highest tensile, tear, and burst indexes and brightness.
- Production enhancement of bioethanol by supplementing vitamins. (June 21- December 21)
 - ✓ Examine the effects of biotin, thiamine, and pyridoxamine on bioethanol production and the mitigation of contamination in molasses. The UV-vis spectroscopy was utilized

- to measure the cell density of baker yeast on a molasses medium. A colony counter was used to count the yeast's colony-forming unit (CFU).
- Production enhancement of baker yeast using orange peel as a biocatalyst and observing the effect of the antimicrobial component, D-limonene. (February 21- April 21)
- ✓ Investigating orange peel behavior as a biocatalyst to boost baker yeast production.

PUBLICATIONS

Patents:

- **Raby, H. S.,** Mohammad, M. G. Thermally Sintered Aluminum Composites with Low Melting Point Metals for Hydrogen Production Through Water Splitting Reaction (Submitted).

Journal Article:

- **Raby, H. S.,** Saadat, M. A., Sakib, A. N., Moni Chowdhury, F., & Yousuf, A. (2024). Bioethanol production from sugarcane molasses with supplemented nutrients by industrial yeast. *Biofuels*, 15(2), 129-135.
- **Raby, H. S.,** and Mohammad, M. G. Thermally Sintered Aluminum Composites with Low Melting Point Metals for Hydrogen Production Through Water Splitting Reaction (Submitted).
- **Raby, H. S.,** Rahman. M. M., Mohammad, M. G., and Siddiquee, M. N. Oxidative depolymerization of polyethylene, polypropylene, and nylon. (Submitted)
- Ahmed, S. R., Murad, A. B., **Raby, H. S.,** Hamid. K., Zaman M. S., Yousuf, A. Advancing in Rice Straw Pulping: A comparative study between kraft and organosolv pulping of silica deposition over rice straw fiber. (Submitted)

Book Chapter:

- Ahmed, S. R., Murad, A. B., **Raby, H. S.**, and Shehab, A. U. Protonic ceramic fuel cell applications. P. Kazempoor, C. Duan & A. Yousuf (Eds). Protonic Ceramic Fuel Cells: Principles, Design, and Application. Elsevier. (Accepted)

POSTER PRESENTATION

Chemical Innovation, Technology and Engineering conference, KFUPM, Dhahran, KSA (April, 2025)

“Thermally Sintered Aluminum Composites with Low Melting Point Metals for Hydrogen Production Through Water Splitting Reaction”.