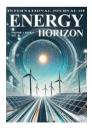


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Research Paper

Utilization of Aluminium for Hydrogen Production: A Sustainable and In-Situ Approach

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ABSTRACT

The production of hydrogen from affordable and widely available resources is necessary for the broader adoption of hydrogen as a sustainable energy carrier. Aluminium, because of its significant energy content per unit mass, natural abundance, and recyclability, has attracted significant attention as a reactive material for on-demand hydrogen generation when combined with water or reducing agents such as sodium borohydride (NaBH4) and hydrogen chloride (HCl). Furthermore, aluminium scraps are a valuable resource which can be used to produce various useful products such as hydrogen, alumina, potash alum, etc. A major limitation in utilising aluminium for hydrogen production is the development of a stable oxide layer (Al_2O_3) on its outer layer, which inhibits its reaction with water. To overcome this barrier and improve hydrogen yield, various activation techniques have been explored. This review critically examines several activation methods aimed at enhancing the reactivity of aluminium, including salt-assisted activation, metal-assisted activation, particle size reduction, etc. The study concludes with a discussion on future directions, emphasising the need for environmentally friendly activation strategies, reusable reaction systems, and integration with aluminium scrap recycling and renewable energy systems to support sustainable hydrogen production.

1. INTRODUCTION

The growing global population and enhanced living standards have led to a substantial rise in energy demand. Although the majority of current energy needs are met through fossil fuels, their limited availability and the environmental issues they cause have highlighted the urgent need for alternative energy sources. Renewable resources like solar and wind offer cleaner alternatives, but their intermittent and location-dependent nature has limited their large-scale deployment. Despite these challenges, reliance on renewable energy sources is growing rapidly (as shown in Fig. 1) [1]. In response to these concerns, extensive research has been conducted to identify clean, reliable alternatives to traditional fossil fuels. Hydrogen is one of the most promising alternative energy options, as it produces only water during combustion, making it an environmentally friendly fuel. This clean characteristic has attracted significant interest, with ongoing focus on improving and optimising hydrogen production methods.

In contrast to conventional batteries, a fuel cell operates like a continuous "factory" for redox-based energy conversion. While energy storage devices such as lithiumion, lead-acid, and manganese-based batteries can only deliver energy for a limited period before needing recharging, fuel cells continue to generate electricity as long as fuel is supplied. Similarly, internal combustion engines also function continuously, but they involve complex steps to convert chemical energy into

mechanical and then into electrical energy. In contrast, fuel cells directly convert chemical energy into electrical energy, resulting in higher overall efficiency. These advantages make fuel cells a promising and commercially viable energy technology, prompting extensive ongoing research. The fundamental reaction in a fuel cell is as given in equation (1).

$$H_2(g) + 0.5 O_2(g)$$
 $H_2O(g) + Heat$ (1)

Figure 1. Global renewable electricity generation [1]

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Hydrogen has a very high gravimetric energy density of 120 MJ/kg, which is about three times that of gasoline (44 MJ/kg), making it an excellent energy carrier by weight. However, its volumetric energy density is significantly lower (approximately 0.01 MJ/L) compared to 32 MJ/L for gasoline. This low volumetric density presents a major challenge for practical applications. Therefore, developing high-density hydrogen storage methods is crucial for improving the overall performance and feasibility of hydrogen-based systems, including proton exchange membrane (PEM) fuel cells [2-10].

Recent research has explored the potential of multinary semiconductors for converting solar energy into hydrogen effectively [11]. Additionally, ammonia borane has been considered a viable hydrogen source because of its high hydrogen content (over 19.6 wt%) and ability for regeneration. Although the release of ammonia as a by-product leads to corrosion of both containers and catalysts, significantly reducing performance (around 95 Wh/kg), which is much lower than that of the sodium borohydride (NaBH₄) system (200-400 Wh/kg). Moreover, ammonia borane can act as a catalyst poison, limiting its applicability in fuel cell systems [9, 12-14]. In contrast, formic acid presents several advantages as a hydrogen carrier. It offers a high volumetric hydrogen capacity (53 g H₂/L), low toxicity, and low flammability in ambient conditions, making it a safer and more practical option for hydrogen storage and transport.

Although lithium-ion batteries are the leading technology for energy storage at present, they have several limitations, including lower power density, safety concerns, limited life, long recharging times, high cost, and limited design flexibility. These drawbacks have driven the search for alternative energy systems with better overall performance. Fuel cells have emerged as a strong option in this regard. They convert chemical energy directly to electrical energy with high efficiency and emit only water as a by-product. Additionally, fuel cells have no moving parts, offer potentially long operational lifetimes, and their energy output is not constrained by the physical size of the cell, unlike batteries. Despite these advantages, the widespread adoption of fuel cells is challenged by factors such as high cost, moderate power density, efficiency limitations, and lifespan issues. Furthermore, fuel accessibility, storage methods, and the required operating temperatures add to the complexity of fuel cell systems. A typical proton exchange membrane (PEM) fuel cell setup includes three main components: a fuel cell stack, a hydrogen generator, and a hydrogen storage unit. Hydrogen is fed to the anode of the fuel cell by the storage unit, and the performance of the cell is influenced by the hydrogen purity, back pressure, and flow rate [15,16]. In recent years, chemical hydrides have gained attention as promising hydrogen storage materials considering their stability at ambient conditions and potential to liberate hydrogen instantly through chemical breakdown. Common hydrides comprise alanate hydrides, alkali metal hydrides, and metal hydroborates, with compounds such as NaBH₄, Zn(BH₄)₂, Ca(BH₄)₂, LiAlH₄, and NaBH(OCH₃)₃ being the most studied. Among them, sodium borohydride (NaBH₄) stands out due to its relatively lower cost and high hydrogen content (10.6 wt%). However, its hydrolysis reaction produces sodium metaborate NaBO2, and a removal or recycling system is essential for practical applications [17]. In addition to chemical hydrides, various organic compounds have also shown potential for high-rate and efficient hydrogen production. However, their commercialisation is limited by the need for expensive catalysts [18].

Water is an abundant and cost-effective source of hydrogen, offering a high hydrogen content. Aluminium (Al), on the other hand, is widely available in the Earth's crust and possesses a range of desirable physical and chemical properties. These include lower density (2700 kg/m³), high hardness, excellent ductility, strong thermal and electrical conductivity, naturally anti-corrosive, and high reflectivity. Due to these characteristics, aluminium has gained attention as a potential energy carrier. Its ability to resist corrosion is largely due to the formation of the stable oxide layer, which is both non-toxic and colorless. Moreover, aluminium can be converted into porous sodium alanate (NaAlH₄), a material that serves as an effective medium for hydrogen storage [19-21].

Hydrogen can be produced through various methods, including thermochemical, electrolytic, solar, and biological processes. However, current green hydrogen production technologies still face problems in terms of efficiency and cost-effectiveness. For instance, photovoltaic electrolysis cells remain uneconomical. Currently, the major portion of hydrogen is generated through hydrocarbons and alcohol reforming [22], coal and fossil fuels gasification [23-26], water electrolysis [27], renewable energy-based systems [28], thermochemical cycles, electro-thermochemical (hybrid thermochemical) cycles and alternative approaches like aluminium-based methods [29-40], ammonia reforming [41], and plasma reforming [42-44]. Among these, the reforming of hydrocarbons and alcohols such as alkanes, alkyl alcohols, and glycerol is commonly carried out using auto-thermal reforming and partial oxidation techniques. However, partial oxidation is challenged by a lower hydrogen-to-carbon monoxide ratio, complex operational requirements, and the need for high operating temperatures [45]. Auto-

thermal reforming, which involves oxygen consumption, is generally not costeffective and therefore has limited commercial application [3,45]. In coal gasification, various coal types are converted into syngas by reacting them with air, steam, or oxygen at elevated temperatures (>900 °C) in a gasifier [24]. This process suffers from low efficiency due to the carbon-rich feedstock and is also associated with high greenhouse gas (GHG) emissions [3,46]. Electrolysis, although a clean method of hydrogen production, demands high electrical energy input and involves the use of expensive membranes, which increases operational costs [47]. Aluminium-based hydrogen production methods involve reactions between aluminium and water or acids, often with the addition of inhibitors to control the process [29-40]. The general aluminium hydrolysis and hydrochlorination reactions are given in (2), (3), and (4) [48,49]. According to reactions (2) and (3), the absolute hydrolysis of 1 gram of aluminium in a nonacidic medium can produce approximately 1245 mL of hydrogen gas at normal temperature and pressure (NTP). The by-products of this reaction, i.e. aluminium hydroxide (Al(OH)₃) and aluminium oxyhydroxide (AlOOH), are stable, amticorrosive, and serve as valuable raw materials for the ceramics and related industries. Hydrogen produced through this route is influenced by the alkalinity of the solution and can be regulated by adjusting the reaction temperature [20]. These reactions are most effective when aluminium is in fresh or activated form, which enhances its reactivity. Furthermore, integrating a hydrogen/air sub-cell into the system has been shown to increase the maximum power output by up to 20% [50]. While these methods offer simplicity and utilize abundant resources, they suffer from uncontrolled hydrogen release due to the exothermic nature of the reactions, which can pose safety and efficiency challenges. In this study, we focus on the direct production of hydrogen with an in-depth discussion on the underlying mechanism. The techniques employed to enhance aluminium reactivity for more efficient hydrogen generation.

$$2AI + 4H_2O \longrightarrow 2AIOOH + 3H_2$$
 (2)

$$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2$$
 (3)

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$
 (4)

2. ACTIVATION OF ALUMINIUM

Due to the presence of an oxide layer on the aluminium surface, the aluminium should be activated, or the oxide layer should be removed to increase the surface area for reaction. Various methods are available, which are discussed in this section

2.1 Aluminium Activation by Gallium-Indium

High intensity energy (HIE) processing of aluminium (Al) powder using a Gallium (Ga)-Indium (In) eutectic alloy, using a planetary ball mill at 220 rpm for 3 minutes, significantly enhanced the metal's reactivity toward water. The milling process employed a steel ball having a diameter of 6 mm, with a powder-to-ball mass proportion of 1:30. In contrast, low intensity energy (LIE) processing involved manually mixing the Ga-In alloy powder in Al powder using a ceramic mortar in a nitrogen gas atmosphere. The results revealed a significant difference in hydrogen generation rates between the two methods. LIE-treated aluminium achieved the highest hydrogen production rate of 11 mL/min, while the HIEtreated sample generated a substantially higher rate of 1.28 L/min when 1 g of Al is used. Although the eutectic Ga-In alloy improved the reactivity of aluminium, it also led to increased brittleness in the material. Temperature was found to significantly impact hydrogen generation in both cases. For LIE-treated aluminium, the hydrogen generation rate improved with temperature, with values of 11 and 95 mL/g/min at 24 °C to 61 °C, respectively. Similarly, for HIE-treated aluminium, the yield was enhanced from 1.28 to 2.60 L/g/min when the temperature rose from 21 °C to 59 °C [51-54].

A detailed investigation was carried out to evaluate the optimal temperature and pressure conditions for activating aluminium using Ga-In alloy. The results revealed that the formation of aluminium oxyhydroxide is thermodynamically beneficial at ambient pressure and temperatures more than 21 °C. In contrast, the formation of aluminium hydroxide is achievable by maintaining the reaction at lower temperatures or under higher pressure. By carefully adjusting the reaction conditions, water consumption in the system can be decreased up to 33.3% with no effect on the overall hydrogen production. This is achieved by directing the reaction pathway toward the formation of AlOOH. Furthermore, by manipulating the operating parameters, different by-products can be selectively produced, each with distinct industrial applications [55].

2.2 Size of Particles

Aluminium powders of both nano and micro scale sizes can interact with water under atmospheric pressure and moderate temperatures for hydrogen generation. Nanosized Al particles are capable of reacting completely with water even at 20 °C, while micro-sized Al particles require a temperature above 40 °C for effective hydrogen generation. This indicates that smaller Al particles can initiate hydrogen production without the need for any prior activation or surface reformation. Initially, the reaction is governed by the accessible surface area of the Al particles, while in later stages it is controlled by the diffusion of water molecules through the by-product layer formed on the particle surface. The induction time for the onset of the reaction depends on the hydrogen diffusion within the bulk aluminium and the critical pressure of gas in hydrogen bubbles formed at the Al/Al₂O₃ interface. It has been observed that the activation energy for the reaction increases with the average size of the aluminium particles, likely due to the broader particle size distribution associated with larger particles. The reaction by-products may include baeyerite, boehmite, or a combination of both, and their composition is influenced by the temperature at which the reaction takes place [32].

Aluminium powders produced through ball milling have demonstrated an exceptionally high capacity to generate hydrogen from aqueous solutions, even at balanced or near-balanced pH levels. Studies have demonstrated that ball milling aluminium with various additives such as sodium hydroxide (NaOH), cobalt oxide (CoO), and molybdenum oxide (MoO₃) significantly alters the morphology and microstructure of the Al particles. These structural changes are highly dependent on the milling duration and operating conditions. One of the key factors contributing to the enhanced hydrogen generation is the increase in the specific surface area of the aluminium particles. For instance, after 15 minutes of ball milling, the specific surface area of Al was observed to be enhanced dramatically from 0.30 m²/g to 9.68 m²/g, thereby promoting more efficient water-splitting reactions. Prolonged ball milling of aluminium decreases the interlayer spacing among particles, resulting in lower reaction rate with water [56].

The proportion of Al to NaCl while milling also plays a significant role in hydrogen generation. A higher concentration of salt was found to enhance the reaction rate, with the maximum average hydrogen production rate recorded at 75 mL/min per gram of Al for an Al to NaCl molar proportion of 5:1. This formulation exhibited 100% conversion within 40 minutes [57]. Activated aluminium powder, produced by mechanical pulverisation of Al with silicon powder, graphite powder, bismuth powder, and NaCl, was effectively utilised for hydrogen production. The powder with an optimal Al to salt molar proportion of 0.5 was not only highly reactive but also suitable for long-term air storage. It demonstrated average hydrogen generation rates of approximately 101 mL/g/min and 210 mL/g/min at initial water temperatures of 55 °C and 70 °C, respectively. When a bismuth alloy was used, the highest rates observed were about 287 mL/g/min and 713 mL/g/min at 55 °C and 70 °C, respectively [58]. In parallel research, mesoporous alumina catalysts with well-managed pore structure were synthesised through the regulated hydrolysis of aluminium alkoxides. Using water to alumina ratios between 2 and 15, various alumina compositions were developed. After calcination at 700 °C for 2 hours, these supports exhibited surface areas of 240-320 m²/g, average pore sizes of 4-18 nm, and pore volumes of 0.4-1.6 mL/g [59]. Hydrogen production through aluminium oxidation was also demonstrated using water vapour, hydrogen peroxide solutions, and water/oxygen mixtures. Water was found to inhibit surface passivation of aluminium when oxygen was introduced. The formation and expansion of oxide and hydroxide nanoparticles during water oxidation advanced the oxidation front deeper into the aluminium. To ensure safety, the molar ratio of O2 to H2 was limited to 13% to prevent excessive hydrogen accumulation and the risk of explosion [60].

2.3 Impact of Zinc or Mercury Amalgamation and Al(OH)₃

The aluminium hydrolysis can be effectively operated at temperatures below 65 °C by employing amalgamation with mercury or zinc. This process significantly enhances the hydrogen generation rate, which increases with temperature. The maximum hydrogen evolution rate recorded was 7.25 L/min at 65 °C for aluminium coated with a zinc conglomerate. Among the two, zinc demonstrated a superior activation effect compared to mercury. This is attributed to its lower activation energy requirement of 43.4 kJ/mol for zinc coating versus 74.8 kJ/mol for mercury. Notably, the by-product formed during this reaction, bayerite, is nontoxic and environmentally safe [61]. Finely divided and poorly crystalline Al(OH)₃ powder has proven to be an effective additive for enhancing hydrogen production in the Al-H₂O system. The proposed mechanism of action involves a reaction given in (5) with a Gibbs free energy change of 39.40 kJ/mol. The surface area of Al(OH)₃ plays a major role in influencing the hydrogen yield, with finer particles yielding better performance. By leveraging an on-demand, self-driven exothermic reaction using a relatively large amount of aluminium (3 g Al to 15 g H₂O) and a minimal amount of fine β-Al(OH)3, approximately 70% hydrogen conversion was

achieved within 30 minutes. Importantly, this approach eliminates the need for high alkalinity and does not cause corrosion-related issues [39].

$$Al_2O_3 + Al(OH)_3 \longrightarrow 3AlO(OH)$$
 (5)

2.4 Carbon Nanoparticles (CNTs), Composites, Graphene/Graphite

The hydrogen production rate was observed to improve with the incorporation of carbon nanotubes (CNTs) into the aluminium matrix. CNTs act as localised cathodic sites during the hydrolysis process, facilitating rapid hydrogen production via galvanic corrosion between the CNTs and the aluminium matrix. Although carbon-based by-products arise from the interaction of carbon and water. Yet, no carbon monoxide (CO) generation was found [62]. Al@rGO (aluminium-reduced graphene oxide) composites, synthesised via ultrasonic atomization, demonstrated significantly enhanced hydrogen generation upon exposure to pure water under infrared irradiation. The presence of reduced graphene oxide not only accelerates the reaction but also provides ~4nm diffusion pathways for efficient transport of reactants and products [63]. Similarly, Al/graphite core-shell composites made from ball milling exhibited effective hydrogen production. When 23 wt% graphite was added, approximately 76.5% of the aluminium content reacted with water to produce hydrogen within 6 hours. An increased reaction temperature enhanced the hydrogen evolution rate, achieving a maximum of 40 ml/g.min Al at 75 °C [64].

Additionally, composites made from bismuth nanoparticle-modified graphene oxide (BiNPs@GO) and bismuth nanoparticles (Bi-NPs), synthesised through hydrothermal processing, showed further improvements in hydrogen generation performance. This enhancement is attributed to the synergetic effects of graphene and nano-bismuth, and notably, the system remained effective even at 0 $^{\circ}$ C. such composites are promising for hydrogen generation in fuel cells operating under variable temperature and pressure conditions [65].

2.5 Other Agents

The use of water-soluble inorganic salts (such as NaCl and KCl) during milling effectively minimises aluminium passivation in the pH range of 5 to 9. Higher concentrations of these salts, along with smaller aluminium particle sizes, significantly enhance the extent of aluminium reacting with water. Additionally, elevated temperatures not only improve the hydrogen generation rate but also lessen the induction time required to initiate the reaction. Based on the hydrolysis reactions that form aluminium hydroxide and baeyerite, approximately 1446 mL of hydrogen can be generated by just 1 gram of aluminium [30]. Alloy ingots composed of Al-Ga-In-Sn₄-Cu have been reported to exhibit superior hydrogen yield and faster production rates compared to Al-Ga-In-Sn₄ alloys. The addition of copper plays a critical role by inhibiting the development of aluminium grains and promoting the pulverisation of the Al(Ga) solid solution. This process increases the surface area available for reaction, thereby enhancing the reactivity of the alloy with water and improving hydrogen production [66].

The activation energy needed for the Al-20%Li alloy was significantly lower than that of the Al-20%Mg alloy. Consequently, Al-20%Li exhibited a hydrogen generation rate of 309.74 mL/g/min and the maximum hydrogen production of 1038 mL/g. In contrast, the yield achieved from Al-20%Mg is found to be approximately 60% of that produced by the Al-20%Li alloy [67]. The addition of CaO and Li/Li₂O to aluminium systems was found to greatly increase hydrogen generation. This improvement is attributed to a decrease in activation energy and the autocatalytic properties of the by-product (Al(OH)3) generated during the process [68]. Al-based composites synthesised from ball milling mixtures of Al, CaO, and salt powder have also been explored for hydrogen generation. A rise in the content of CaO and NaCl was shown to be favourable, and the highest hydrogen yield was achieved at 30 °C [69, 70]. Incorporating hydrides into aluminium-based materials further improved hydrogen generation performance, with lithium hydride (LiH) demonstrating the best results. An Al-30 mol% LiH sample, milled for 3 hours, achieved a hydrogen yield of 96.3% and a peak generation rate of 4556.3 mL/g.min at 75 °C [34, 71]. Additionally, hydrolysis of waste aluminium in a mildly alkaline solution (~70 °C) using Ni or Ni/Bi additives produced impressive results. This setup achieved a hydrogen generation rate of 9.00 L/g/min and an overall yield of 1.35 L/g, having nearly a 100% conversion rate [72].

Bismuth-based composites have demonstrated effective activation properties, and the Al-Bi $_2$ O $_2$ CO $_3$ system, prepared via ball milling, has been successfully employed for hydrogen generation. The hydrogen production efficiency was influenced by several factors, including the Bi $_2$ O $_2$ CO $_3$ content, ball milling duration, and the powder-to-ball ratio. The hydrolysis reaction yielded by products such as Bi $_2$ O $_2$ CO $_3$, AlO(OH), and Al $_2$ O $_3$. Doping the Al-15 wt% bi $_2$ O $_2$ CO $_3$ composite with 5 wt% of NaCl or AlCl $_3$ effectively eliminated the induction period and significantly enhanced both the hydrogen yield and

generation rate. The initial temperature of the reaction influenced the rate of hydrogen production, though it had a minimal effect on the overall yield. Additionally, the reaction yield was affected by the ageing time of the composite when exposed to air [73].

2.6 Aluminium Reaction with Steam

Shmelev et al. performed an experiment to generate hydrogen by hydrolysis of molten Al (900-950 °C) in a reactor [74]. They used a stainless-steel reactor with a diameter of 42 mm and a height of 82 mm. A maximum of 40% hydrogen yield was observed, which was increased to 100% by adding 10% KOH in molten Al. Furthermore, it was concluded that the reactor could produce a maximum of 13 L of hydrogen per minute from 1 L of the melted Al. Gao et al. investigate the characteristics and working mechanism of aluminium-gas water and aluminiumliquid water reactions at temperatures ranging from 250-376 °C and pressures between 4.0-23.5 MPa [75]. They found that supercritical steam showed strong reactivity, inhibiting passivation, with 8 mm aluminium particles completely oxidised at 376 °C and 23.5 MPa. However, steam-based hydrogen yield was observed to be slightly less or equal when compared to liquid water-based reactions due to differences in working mechanisms and aluminium surface contact opportunities. Wang et al. demonstrated the hydrogen production behaviour of millimetre-sized aluminium spheres reacting with subcritical and supercritical water, without the use of any additives or catalysts [76]. The effect of reaction time, temperature, and aluminium sphere size on hydrogen generation is systematically analysed. The results reveal that the aluminium-water reaction proceeds through four distinct stages, with hydrogen production increasing over time. For a 6.35 mm aluminium sphere, a maximum hydrogen yield of 86.7% is achieved at temperatures between 550-600 °C. Furthermore, reducing the aluminium sphere size significantly enhances reactivity. Spheres with a diameter of 2.38 mm attain a hydrogen yield of up to 95% and a reaction ratio of 91.71%. These findings suggest that the reaction between millimetre-sized aluminium and sub/supercritical water holds potential for integrated hydrogen, heat, and electricity generation systems.

3. CONCLUSION

This review highlights the potential of aluminium (Al) for hydrogen production, with surface passivation identified as a key barrier to efficient Al-water reactions. Various strategies and conditions that enhance Al hydrolysis have been thoroughly examined. Among the promising approaches, mechanically milled Al nanoparticles (~4nm) combined with NaCl at an Al-to-salt ratio of 0.5 demonstrated both cost-effectiveness and high performance, yielding 101 ml H₂/g/min at 55 °C and 210 ml H₂/g/min at 70 °C. The inclusion of carbon-based materials significantly improved hydrogen output. The type of aluminium precursor, such as mesoporous/microparticle Al, Al(OH)₃, Al₂O₃ and AlCl₃, also influenced the yield positively. Additives like NaCl, KCl, CaO, carbon nanotubes (CNTs), and graphene further enhanced hydrogen generation. Surface activation through amalgamation with Zn or Hg, and alloying with elements such as Bi, Sn, Ga, In, and Cu, notably increased reactivity and hydrogen yield. The use of waste Al as a hydrogen source was also explored, with galvanic corrosion promoted by elements like Bi and Ga playing a significant role. Since these metals are expensive, alternatives should be explored, despite their recyclability. Key challenges remain in scaling this technology, particularly in managing the accumulation of hydrolysis by-products such as Al(OH)3 and AlOOH, which form surface deposits and inhibit reaction progress. Efficient removal strategies for these by-products and for excess heat generated during the reaction must be developed. Finally, integrated studies combining the most effective approaches discussed in this review are necessary to overcome current limitations and advance aluminium-based hydrogen generation technologies.

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