

A Green Energy Closed-Loop System Based on Aluminum

Hong-Wen Wang ^{1,*} and Liang-Ying Huang ²

¹ Department of Chemistry, Chung-Yuan Christian University, Chungli, Taoyuan 320, Taiwan

² Department of Optics and Photonics, National Central University, Chungli, Taoyuan 320, Taiwan; gstech5219@gmail.com

* Correspondence: hongwen@cycu.edu.tw

Abstract

This paper presents a focused review of a closed-loop system for sustainable hydrogen production utilizing the reaction between metallic aluminum powders and water, coupled with renewable energy-driven recycling of aluminum hydroxide (or alumina) by-products back to metallic aluminum powders. A green energy closed-loop system based on aluminum could be achieved if the converting process is accomplished by a green Hall–Héroult process, where a cermet inert anode was used. Meanwhile, the byproduct alumina is converted back to the liquid form of aluminum at high temperature (up to 960 °C), producing pure oxygen. A high-pressure atomization process is then used to break the aluminum droplets into powder using argon gas. The technical feasibility, thermodynamic efficiency, economic viability, environmental sustainability, and comparison of this green aluminum cycle with existing hydrogen production and energy storage technologies are discussed. The aluminum–water reaction offers exceptional energy density (29.7 kJ/g of Al), ambient temperature operation, and zero direct carbon emissions. However, commercial implementation faces substantial challenges including overall round-trip energy efficiency (estimated 34.5–46.6%), technological maturity of the recycling process, passivation layer management, and economic competitiveness with conventional water electrolysis. Despite these challenges, the system demonstrates advantages for seasonal energy storage, off-grid applications, and integration with intermittent renewable energy sources. This analysis provides a framework for researchers, engineers, and policymakers to assess the potential role of aluminum-based energy cycles in the global energy transition toward carbon neutrality.

Keywords: green hydrogen; aluminum–water reaction; closed-loop energy system; renewable energy storage; circular economy; carbon neutrality

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1. Introduction

The urgent need to mitigate climate change has positioned hydrogen as a cornerstone of the global energy transition. As nations commit to ambitious carbon neutrality targets, “green hydrogen”—produced exclusively through renewable energy-driven processes—has emerged as a critical enabler of deep decarbonization across transportation, industry, and power sectors [1–6]. Global decarbonization efforts are increasingly investigating diverse hydrogen production pathways, including bio-oil gasification and steam reforming of various biomass residues [7–9]. However, conventional green hydrogen production via water electrolysis faces persistent challenges: high capital costs (currently 6–8 USD/kg H₂), substantial electricity consumption (50–55 kWh/kg H₂), infrastructure requirements for

storage and distribution, and dependence on high-purity water resources [10,11]. In parallel, the intermittency of renewable energy sources (solar and wind) necessitates large-scale, long-duration energy storage solutions. While lithium-ion batteries excel at short-duration applications, seasonal energy storage demands fundamentally different approaches. Hydrogen storage, whether as compressed gas (350–700 bar), liquid (−253 °C), or chemical carriers such as AlH_3 [12], presents technical and economic barriers that limit widespread deployment [13].

Recent advances in materials science and electrochemistry have renewed interest in metallic aluminum as a recyclable energy carrier and hydrogen source [14–17]. The aluminum–water reaction for hydrogen generation, first explored in the early 20th century, has gained significant momentum due to several compelling attributes [18,19]:

1. **Exceptional energy density:** Aluminum possesses a volumetric energy density of approximately 23.5 MWh/m³, surpassing compressed hydrogen (700 bar: 1.6 MWh/m³), liquid hydrogen (2.4 MWh/m³), and lithium-ion batteries (0.5–0.9 MWh/m³) [16–20]. While the volumetric energy density and stability of aluminum are technically superior to other energy carriers, its true value lies in its ability to bridge critical gaps in renewable energy supply chains. By acting as a high-density ‘solid fuel,’ aluminum facilitates the spatial decoupling of renewable energy generation centers (e.g., solar-rich arid regions) from industrial demand, providing a resilient solution for long-haul energy logistics where compressed hydrogen infrastructure is impractical.
2. **Safe and stable storage:** As a solid metal, aluminum requires no pressurization, cryogenic cooling, or active thermal management. It exhibits zero self-discharge over indefinite storage periods, making it ideal for seasonal energy storage applications [21,22].
3. **Abundant and recyclable:** Aluminum constitutes 8.1% of the Earth’s crust, ranking as the second most abundant element on Earth. Global aluminum production and processing infrastructures are mature and geographically widespread. Aluminum recycling is particularly well established, with recycling rates exceeding 75% in sectors such as transportation and construction, significantly reducing both energy consumption and lifecycle carbon emissions [6]. When recycled, aluminum requires only about 5% of the energy needed to produce it from its ore. Thus, promoting recycling alongside the transformation of aluminum compounds fosters a more sustainable future.
4. **On-demand hydrogen generation:** The aluminum–water reaction proceeds at ambient temperature and pressure, eliminating the need for high-pressure storage infrastructure and enabling decentralized, on-site hydrogen production. When coupled with renewable energy-driven electrolytic reduction of aluminum hydroxide or alumina (the reaction byproduct) back to metallic aluminum, this creates a unique “aluminum–hydrogen cycle” that functions simultaneously as a hydrogen production technology plus a long-duration energy storage medium plus a circular materials economy.

Unlike lithium-ion batteries, which are optimized for short-duration frequency regulation and daily cycling, the aluminum–hydrogen cycle is uniquely positioned as a long-duration seasonal energy storage medium. While early research explored its use in various sectors, its primary competitive niche is the temporal and spatial decoupling of massive renewable surpluses from high-demand winter heating or heavy-duty industrial cycles.

As shown in Figure 1, aluminum could serve as a green energy storage medium if the processes described in the following paragraphs can be realized. In this study, ‘green aluminum’ refers specifically to metal produced via renewable-powered electrolysis using inert anodes. The term ‘closed-loop’ signifies the near-complete (>95%) recovery and recycling of aluminum byproducts, while ‘carbon neutral’ denotes a system where the lifecycle CO₂ emissions match or beat direct renewable water electrolysis (0.5–2.0 kg CO₂/kg H₂).

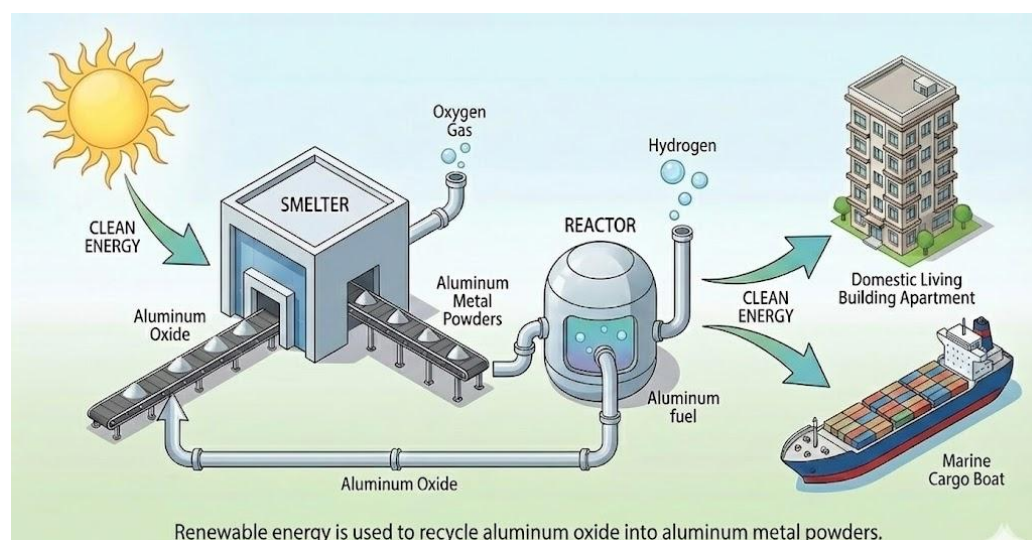


Figure 1. Aluminum as a green energy carrier.

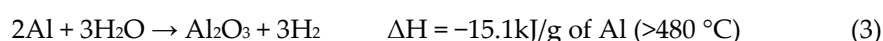
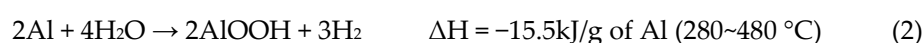
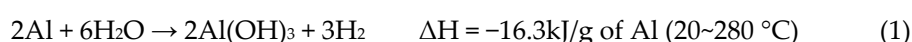
Despite growing research interests, comprehensive techno-economic assessments of the complete aluminum–hydrogen cycle remain limited. A holistic system-level analysis for the closed loop of aluminum is needed. In this study, the ‘aluminum–hydrogen system’ is defined as an integrated energy–material network comprising three core pillars: (1) the industrial energy hub (renewable-powered smelting and atomization), (2) the logistical distribution network (solid aluminum transport and byproduct recovery), and (3) the decentralized end-use reactors (hydrogen and heat generation). This holistic definition acknowledges that while the material loop is closed, the system relies on continuous external renewable energy inputs and a managed ‘reverse supply chain’ for byproducts.

This paper provides an integrated evaluation encompassing the following: 1. Thermodynamic and kinetic analysis: detailed examination of the aluminum–water reaction mechanisms, activation strategies, and hydrogen yield optimization. 2. Energy efficiency assessment: quantitative analysis of round-trip energy efficiency, including losses in aluminum recycling, hydrogen generation, and end-use conversion. 3. Economic viability: cost modeling across the entire value chain, from aluminum production to hydrogen utilization, with comparison to competing technologies. 4. Environmental lifecycle assessment: evaluation of carbon footprint, water consumption, material circularity, and ecological impacts. 5. Comparative benchmarking: systematic comparison with alternative energy storage and hydrogen production technologies across multiple performance dimensions. Through this focus analysis, we aim to provide the scientific community and policymakers with an evidence-based foundation for evaluating the potential role of aluminum-based energy systems in achieving global sustainability goals.

2. Green Hydrogen Production via the Aluminum–Water Reaction

2.1. Reaction Chemistry and Thermodynamics

The hydrogen generation from metallic aluminum and water proceeds through three pathways, depending on reaction conditions such as temperature and pressure [23]:



All reactions are thermodynamically favorable ($\Delta G^\circ < 0$) and highly exothermic. The product of reaction (1) is stable from room temperature up to 280 °C, and the primary byproduct is $\text{Al}(\text{OH})_3$. From 280 to 480 °C, Boehmite, AlOOH , is the thermodynamically favored product, and Al_2O_3 is the major product above 480 °C [23]. The theoretical hydrogen yield is impressive: 1 g of aluminum produces 1.245 L of H_2 at STP, or 1.36 L at room temperature, corresponding to a gravimetric hydrogen storage capacity of 11.1 wt%, i.e., at room temperature, 9 kg aluminum and 18 kg water produce 1 kg hydrogen and 26 kg of $\text{Al}(\text{OH})_3$. The exothermic nature of the reaction presents both opportunities and challenges. While the heat can be recovered for cogeneration applications, excessive temperature rise can accelerate both reaction and passivation layer formation, requiring careful thermal management in the reactor design. Equation (3) also represents an alternative pathway enabled by the high-temperature operation. A Canadian company, GH Power, has utilized this method to produce green hydrogen using aluminum scraps [24]. Since the byproduct is Al_2O_3 at high temperature, it would be the direct raw materials for reduction process, the Hall–Héroult process. This represents an ideal pathway to run this green energy closed-loop system. However, if we consider generating green hydrogen anywhere in an isolated area, where only simple Al–water reactors can be installed at room temperature, $\text{Al}(\text{OH})_3$ will be the major byproduct.

Figure 2a,b show the idea of a closed-loop system based on aluminum. These systems can be considered genuinely green energy closed-loop systems if renewable energy powers all the required electricity.

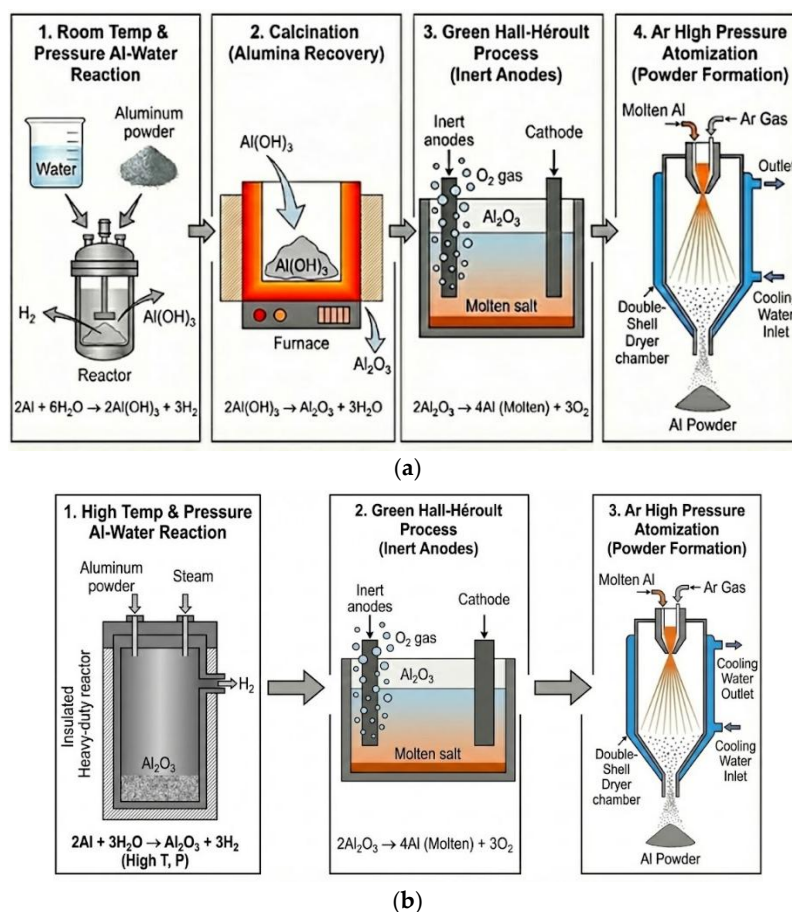


Figure 2. A green energy closed-loop system based on aluminum, (a) hydrogen is released at room temperature, and (b) hydrogen is released at high temperature and high pressure.

2.2. Advantages of Aluminum–Water Hydrogen Generation

The aluminum–water hydrogen generation system exhibits several intrinsic advantages over conventional hydrogen production, storage, and delivery technologies, particularly in terms of energy density, operational safety, environmental performance, and resource availability. As mentioned earlier, aluminum metal possesses an exceptionally high volumetric energy density compared with molecular hydrogen stored in either compressed or liquefied form. Theoretical gravimetric hydrogen yielded from the aluminum–water reaction corresponds to 11.1 wt% hydrogen, which is comparable to or higher than that of many advanced chemical hydrides. Unlike electrochemical energy storage systems, aluminum metal can be stored indefinitely under ambient conditions without energy loss, owing to its intrinsic chemical stability and absence of self-discharge [16–20].

The aluminum–water reaction can be carried out at or near room temperature and atmospheric pressure, eliminating the need for high-pressure compression or cryogenic liquefaction infrastructure typically required for hydrogen storage and transportation. From a safety perspective, solid aluminum is non-flammable and non-explosive, in contrast to gaseous or liquid hydrogen, which poses significant risks associated with leakage, embrittlement, and ignition. Furthermore, aluminum can be transported and stored using conventional freight and handling systems, substantially reducing logistical complexity and cost [16–22].

The aluminum–water reaction produces hydrogen gas and aluminum hydroxide at temperatures below 100 °C, or aluminum oxide at temperatures above approximately 480 °C, without emitting greenhouse gases or toxic byproducts during hydrogen generation [23]. The solid reaction product, aluminum hydroxide ($\text{Al}(\text{OH})_3$), is a valuable industrial material widely used in ceramics, water treatment, flame retardants, fillers, and pharmaceutical applications, and can be readily converted into alumina (Al_2O_3) via controlled dehydration.

When integrated with renewable energy-driven aluminum recycling—such as the green Hall–Héroult process employing inert anodes [25–28]—the aluminum–water system enables a near-closed, low-carbon material and energy cycle, supporting circular economy objectives.

2.3. The Passivation Challenge: Aluminum Oxide Layer Formation

Despite favorable thermodynamics, the aluminum–water reaction faces a critical kinetic barrier: the rapid formation of a dense, adherent aluminum oxide (Al_2O_3) passivation layer on the metal surface. This native oxide layer, typically 3–5 nm thick, forms spontaneously upon exposure to air or water and effectively isolates the underlying aluminum from further reaction. The passivation layer exhibits the following: 1. High chemical stability: resistant to dissolution in neutral pH water. 2. Low ionic conductivity: blocks transport of water molecules and hydroxide ions. 3. Strong adhesion: mechanically robust and difficult to disrupt. 4. Self-healing properties: rapidly reforms if mechanically damaged. This passivation behavior explains why bulk aluminum objects remain stable in water despite the thermodynamically favorable reaction. Overcoming this barrier is essential for practical hydrogen generation and has driven extensive research into activation strategies [20,29–78].

2.4. Activation Strategies for Continuous Hydrogen Generation

Researchers have developed diverse approaches to disrupt or prevent passivation layer formation, enabling sustained aluminum–water reactions. These strategies can be broadly categorized into mechanical, chemical, and hybrid methods.

Low-melting-point metal activators: Gallium (melting point 29.8 °C) and gallium–indium eutectic alloys (melting point 15.7 °C) form eutectic reactions with aluminum and wet aluminum surfaces, disrupting oxide layer continuity and creating electrochemical cells that promote localized corrosion [29–39]. These liquid metal activators demonstrate

high effectiveness and enable a rapid and sustained hydrogen generation. These additives can be recovered and recycled after reaction. However, the gallium costs 200–400 USD/kg and indium 300–600 USD/kg. In addition, the reclaimed byproducts require further treatments before being introduced into the reduction process.

Ball milling and alloying: High-energy ball milling incorporates low-melting-point metals (bismuth, gallium, indium, or tin) or reactive salts into aluminum powder [29,31]. The mechanical process creates fresh, oxide-free aluminum surfaces; introduces grain boundaries and defects that facilitate water penetration; and distributes activating agents throughout the aluminum matrix. Al-Ga-In-Sn alloys can achieve near-complete hydrogen conversion (>95%) within minutes at room temperature [31–33]. However, the cost and recyclability of gallium and indium remain concerns for large-scale applications.

Particle size reduction: Reducing aluminum particle size increases surface area and reduces diffusion distances. Nano-sized aluminum particles (50–200 nm) exhibit dramatically enhanced reactivity, but present challenges in handling, storage stability, and production costs [40]. A shrinking core model was proposed to analyze the reaction progress. The Al–water reaction was controlled by the surface chemical mechanism at the initial stage, and then by the H₂O molecule diffusion in the byproduct layer afterwards. The activation energy was estimated to be 64.2 kJ/mol to 88.7 kJ/mol with increasing Al particle sizes from 98.38 nm to 24.94 μ m [41].

Alkaline activation: Sodium hydroxide (NaOH) or potassium hydroxide (KOH) solutions dissolve the aluminum oxide layer through amphoteric reactions:



While highly effective, alkaline activation introduces several considerations: 1. Cautious handling: Requires corrosion-resistant materials and safety protocols. 2. Byproduct complexity: Produces sodium or potassium aluminate solutions requiring additional processing. 3. pH management: Continuous reaction requires pH control and alkali replenishment [42]. This simple method was widely used in the transformation of waste aluminum into aluminum hydroxides and green hydrogen [43,44].

Nano-sized oxides catalysts: Chemically synthesized nano-sized metal oxides, such as Al₂O₃, AlOOH, or Al(OH)₃, occupy a unique position in enhancing the Al–water reaction [45–60]. While the metal hydroxides are typically viewed as reaction byproducts that contribute to the passivation layer, nano-sized Al(OH)₃ paradoxically induces a potent autocatalytic effect. It has been demonstrated that this enhancement is not merely due to physical abrasion but is driven by a ‘seeding mechanism’ where the specific crystallinity and phase of the Al(OH)₃ additives play a critical role [49–52]. Unlike inert ceramic additives such as TiO₂ or Al₂O₃ [53–57], synthesized Al(OH)₃ nanoparticles—particularly those with poor crystallinity or specific bayerite/gibbsite phases—act as active nucleation sites. These sites lower the energy barrier for precipitation, effectively decoupling the product formation from the aluminum surface. This mechanism prevents the accumulation of a cohesive, blocking gel layer on the metallic core, ensuring continuous water access and sustaining high hydrogen generation rates without the need for corrosive alkaline promoters. However, an alkaline solution does enhance the catalytic effect of Al(OH)₃ [61]. It is believed that the nano-sized Al(OH)₃ creates a local high pH environment even when the solution is only around ~9 pH value for most practical conditions, and the formation of an intermediate, AlOOH, as shown in Equation (5) could critically facilitate the reaction in Equation (6) [54]:



The regenerated Al_2O_3 may consist of nano-sized particles and react with $\text{Al}(\text{OH})_3$ more easily. The remaining $\text{AlO}(\text{OH})$ are not stable in water at room temperature and will be easily transformed to $\text{Al}(\text{OH})_3$.

Carbon-mixed catalysts: Recent research demonstrates that carbon materials (activated carbon, graphene oxide, carbon nanotubes) mixed with aluminum hydroxide can catalyze hydrogen generation [62–64]. The carbon matrix provides conductive pathways for electron transfer and creates micro galvanic cells that promote localized corrosion. It offers high surface area for reaction sites. The synergy between the hydroxide ‘seeds’ and carbon-based modifiers has been shown to further accelerate hydration kinetics, marking synthesized $\text{Al}(\text{OH})_3$ as a critical, green component for sustainable hydrogen production.

Organic activators: A 2024 study showed that imidazole (a caffeine derivative) in seawater dramatically accelerates hydrogen generation from Ga-In-coated aluminum scrap [65]. Imidazole acts as a corrosion inhibitor, bonding through its nitrogen atoms to metal surfaces, which helps protect the Ga-In-Al particles from corrosive elements like chlorides and sulfates in seawater. This protective action allows the reaction to proceed rapidly while safeguarding the alloy. This approach is particularly promising due to the low toxicity of imidazole and abundance, which can be derived from biomass sources. The use of seawater instead of freshwater is also an important advantage for practical purposes, since it has been proved that seawater, while chloride ions promote initiation through pitting corrosion by bonding with Al^{+3} , the complex ionic environment of seawater overall will inhibit the total hydrogen generation rate and yield [66,67].

High-pressure activation: Studies show that elevated pressure (5–20 MPa) can enhance aluminum–water reactions by compressing the oxide layer, creating microcracks, increasing water penetration into grain boundaries, and shifting thermodynamic equilibria favorably. The 1–4 mm aluminum particles achieve 100% hydrogen yield at 350–360 °C and 16.5–18.7 MPa. The supercritical water demonstrates strong reactivity, inhibiting passivation, with 8 mm aluminum particles fully oxidized at 376 °C and 23.5 MPa [68–70]. This approach may enable oxide evolution and aluminum regeneration in integrated systems, though it requires specialized reactor designs.

Metal salts: High-energy ball milling with inorganic salts, particularly sodium chloride (NaCl), serves as a robust mechanical–chemical activation strategy to enhance the hydrogen generation rate of aluminum [71–75]. In these processes, metal salt acts as a critical milling agent that prevents the cold welding of aluminum particles, thereby facilitating significant particle size reduction and increasing the effective surface area available for the reaction. Beyond mechanical refinement, the inclusion of NaCl in composites—such as Al/Ni mixtures or Al-Bi(OH)₃ systems—promotes the formation of defects and pits in the passivation layer, which accelerates water penetration and sustains the reaction kinetics. Recent research has further expanded this approach by utilizing a variety of metal salts to mediate the Al–water reaction or incorporating salts into complex Al alloy/g-C₃N₄ composites [75] to significantly improve low-temperature hydrolysis performance. These salt-based activation strategies offer a practical and lower-cost alternative to specialty liquid metal activators, making them highly attractive for large-scale industrial energy storage applications.

2.5. Reactor Design for Al–Water Reaction at Room Temperature

Practical implementation of aluminum–water hydrogen generation requires careful reactor design addressing [76,77]: 1. Thermal management: Exothermic heat must be removed or utilized to prevent temperature-driven passivation and ensure consistent reaction rates. 2. Hydrogen purity: Generated hydrogen typically contains water vapor and trace contaminants requiring purification for fuel cell applications. 3. Byproduct handling: Aluminum hydroxide precipitates must be continuously removed to maintain reaction

kinetics and facilitate recycling. 4. Scalability: Reactor configurations must transition from laboratory-scale batch reactors to continuous-flow systems for commercial applications. 5. Safety systems: Hydrogen detection, ventilation, and emergency shutdown systems are essential for safe operation.

A simple Al/water reactor based on prior works to demonstrate the idea is shown in Figure 3. A small-sized reactor based on a continuous running idea that the input reactants and output byproducts can automatically operate 7/24 at room temperature. The quantity of hydrogen generated per day is determined by the size of reactors which can be modified according to practical needs.

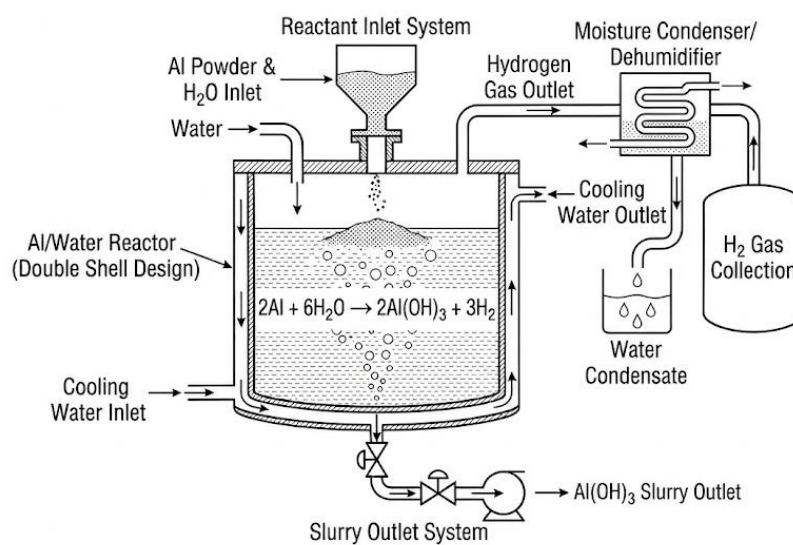


Figure 3. A simple aluminum–water reactor to generate green hydrogen.

State-of-the-art aluminum–water hydrogen generation systems have demonstrated the ability to continuously generate hydrogen with yields exceeding 95% of the theoretical maximum (1.36 L H₂/g Al) under optimized laboratory conditions. A batch of 50 g aluminum could completely be converted to hydroxides in 5–10 min, and release pure hydrogen, and the exothermic heat can be reused. Hydrogen purity over 99.9% can be collected after water condensation. However, for continuous operation of this reaction, automation of the input of reactants and the removal of byproducts requires robust design. While these results are promising, achieving such kinetics at the industrial scale remains a significant engineering challenge requiring further optimization of reactants delivery and heat dissipation.

To manage the intense exothermic heat and dynamic passivation of the Al–water reaction, a digital twin architecture is proposed [78–80]. Digital twin architecture serves as a high-fidelity virtual replica of the physical reactor system, establishing a real-time, bidirectional data link between the operational hardware and a simulation model. By integrating continuous streams of sensor data—such as temperature gradients, pressure, and hydrogen evolution rates—the architecture utilizes physics-based and data-driven algorithms to monitor system health and predict dynamic behaviors, such as the onset of surface passivation. This digital mirror allows for “what-if” scenario testing and the real-time optimization of reactant feed rates, including aluminum powders and water, effectively bridging the gap between static laboratory observations and the complex requirements of dynamic industrial control. This transitions the reactor from a static laboratory batch process to a dynamically optimized industrial unit capable of maintaining steady-state operation under varying load conditions.

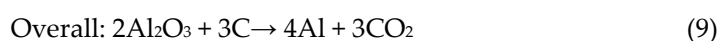
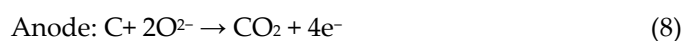
3. Recycling of Aluminum Hydroxide to Metallic Aluminum

The environmental and economic sustainability of the aluminum–hydrogen cycle critically depends on efficient recycling of aluminum hydroxide byproducts back to metallic aluminum using renewable energy. This section examines the recycling process, energy requirements, technological advances, and remaining challenges.

3.1. Aluminum Production

3.1.1. Primary Aluminum Production: The Hall–Héroult Process

The dominant industrial method for primary aluminum production, developed in 1886, involves electrolytic reduction of aluminum oxide (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6) at approximately 960 °C [81,82], where a graphite anode was employed for practical purposes.



Energy requirements: Theoretical minimum: 6.3 kWh/kg Al (based on thermodynamic calculations); practical consumption: 13–15 kWh/kg Al in modern smelters (15.7 kWh/kg industry average) [81]; and energy efficiency: approximately 50% (ratio of theoretical to actual energy consumption).

Carbon footprint: When powered by fossil fuel electricity (global grid average ~500 g CO_2/kWh), primary aluminum production generates approximately 12–16 kg CO_2/kg Al—one of the most energy-intensive industrial processes globally [81]. This carbon footprint can be completely removed if an inert anode and renewable energy is used. We will discuss this in more detail later.

3.1.2. Secondary Aluminum Production: Recycling

Aluminum recycling through remelting requires dramatically less energy. Energy consumption: 0.5–0.8 kWh/kg Al (only ~5% of primary production energy) [6]; carbon emissions: 0.5–1.5 kg CO_2/kg Al (90–95% reduction vs. primary production); and material efficiency: aluminum can be recycled indefinitely without quality degradation. This profound energy advantage makes aluminum recycling one of the most successful circular economy examples, with global recycling rates exceeding 75% in many applications [6].

3.1.3. Inert Anode for Hall–Héroult Process

The carbon anode consumption alone generates approximately 0.8–1.0 tons of CO_2 per ton of aluminum, accounting for a substantial fraction of the total greenhouse gas emissions associated with primary aluminum production. Inert anodes represent a transformative technological solution to this challenge [26–28]. By replacing consumable carbon anodes with chemically stable, electrically conductive materials, the anodic reaction is fundamentally altered. Instead of producing CO_2 , inert anodes enable the direct evolution of oxygen according to the reaction $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + 1.5\text{O}_2$. This change eliminates all direct process-related carbon emissions from the electrolysis cell, enabling so-called “near-zero” or “carbon-free” aluminum production when combined with low-carbon or renewable electricity sources. The comparison of traditional and green Hall–Héroult processes is shown in Figure 4.

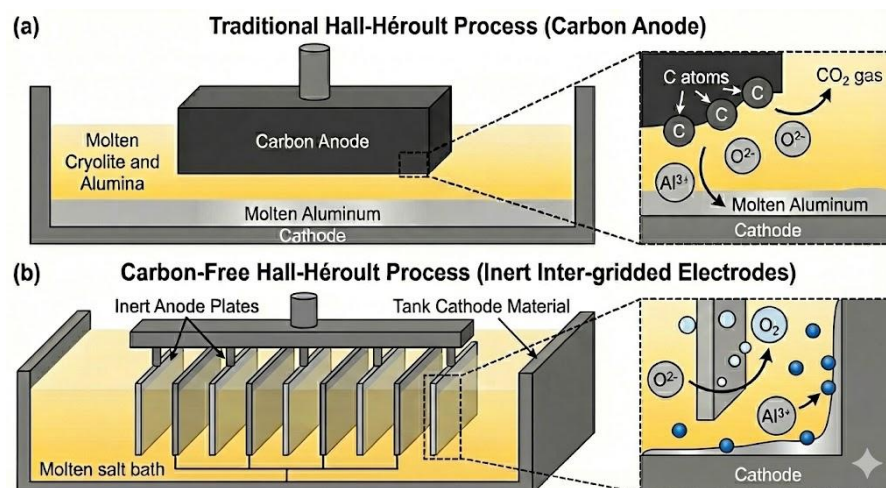


Figure 4. Aluminum electrolysis cells using (a) carbon anodes and (b) inert anodes.

From a systems perspective, inert anodes are a key enabler of “green aluminum” value chains. When powered by renewable electricity, inert anode-based Hall–Héroult cells decouple aluminum production from fossil carbon, allowing aluminum to function as a low-carbon structural material, an energy carrier, and a recyclable metal with minimal lifecycle emissions. As global demand for sustainable materials accelerates, inert anodes will play a central role in aligning aluminum production with long-term climate and circular economy goals.

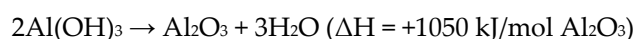
Inert anodes for the Hall–Héroult process are typically based on electrically conductive, corrosion-resistant materials that remain stable in aggressive molten cryolite electrolytes at temperatures near 950–970 °C. The most widely investigated systems include metal–ceramic composites (cermets), particularly those composed of nickel ferrite (NiFe_2O_4) or mixed spinel oxides combined with metallic phases such as Cu, Ni, or Cu–Ni alloys, which provide both chemical stability and sufficient electrical conductivity [26–28]. Alternative approaches involve doped oxide ceramics (e.g., $\text{NiO–Fe}_2\text{O}_3$ -based spinels), as well as metallic alloys protected by in situ formed oxide scales. The key material requirements include high electronic conductivity at operating temperature, low solubility in molten fluoride salts, thermal and mechanical stability, and the ability to form a dense, adherent oxide layer that limits corrosion while allowing oxygen evolution [28].

3.2. Metallic Aluminum Recycling Pathways

The aluminum–water reaction produces aluminum hydroxide ($\text{Al}(\text{OH})_3$) or aluminum oxyhydroxide (AlOOH) or alumina (Al_2O_3), which must be converted to metallic aluminum to close the loop [82]. However, direct electrochemical reduction of $\text{Al}(\text{OH})_3$ (in aqueous or hydroxide media) is extremely challenging because metallic Al is readily re-oxidized by water or OH^- at typical potentials, and aluminum dissolves poorly in aqueous electrolytes. As a result, neutral/alkaline aqueous systems typically cannot support the direct deposition of Al metal because the necessary potential also drives water hydrogen evolution and re-oxidation. Therefore, molten salts or ionic liquids are used instead of water-based electrolytes for Al electrolysis. The following primary pathways exist.

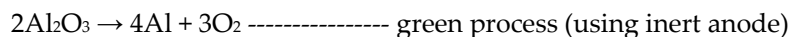
3.2.1. Two-Step Process

Step 1: Calcination (dehydration)



Temperature: 1000–1200 °C; energy requirement: ~1.5–2.0 kWh/kg Al_2O_3 .

Step 2: Conventional or green Hall–Héroult electrolysis



Temperature: 960 °C; energy requirement: 13–15 kWh/kg Al.

Total energy consumption: ~14.5–17 kWh/kg Al (comparable to primary aluminum production).

This conventional route offers no energy advantage over primary production. However, the sustainability of the green closed-loop cycle can be performed by the green process which requires an inert anode as mentioned and energy from renewable sources.

Meanwhile, a wettable cathode plays a crucial role in improving the efficiency and sustainability of aluminum reduction processes. Unlike conventional carbon cathodes, a wettable cathode—most notably based on TiB₂—is uniformly wetted by molten aluminum, allowing the formation of a thin and stable aluminum layer directly on the cathode surface. This feature enables a significant reduction in the anode–cathode distance (ACD), which in turn lowers ohmic resistance and cell voltage, leading to substantial energy savings. Moreover, a wettable cathode stabilizes the metal–electrolyte interface, suppresses metal pad waves, and reduces the risk of short-circuiting, thereby improving current efficiency and operational stability. These advantages are particularly critical for advanced cell designs such as vertical electrode cells and for the integration of inert anodes, where wettable cathodes TiB₂ are essential to offset the higher intrinsic cell voltage and to achieve lower greenhouse gas emissions and reduced specific energy consumption in aluminum electrolysis [83].

3.2.2. Low-Melting Electrolyte for Electrolysis

The development of low-temperature electrolytes, particularly the KF–AlF₃–Al₂O₃ system, represents a significant advancement in the modernization of the Hall–Héroult process [84–101]. By utilizing potassium cryolite (K₃AlF₆) with a cryolite ratio (CR = $n_{\text{KF}}/n_{\text{AlF}_3}$) typically between 1.2 and 1.5, the operating temperature can be reduced from the industrial standard of 960 °C to a range of 700–800 °C. This thermal reduction is primarily driven by the existence of a eutectic point in the binary KF–AlF₃ system at approximately 560 °C. A critical advantage of this potassium-based electrolyte is its superior alumina solubility at lower temperatures; while sodium-based systems lose solubility rapidly below 900 °C, the KF–AlF₃ melt can maintain a sufficient alumina concentration of approximately 5 wt% at 700 °C. Such low-temperature operation is deemed “inert anode friendly,” as it drastically decreases the corrosion rates of metallic and ceramic anodes, potentially enabling carbon-free aluminum production with oxygen as the only gaseous byproduct. However, challenges remain regarding the lower electrical conductivity of K-based melts compared to traditional Na-based baths, which necessitates careful optimization of the bath composition to manage the energy balance and ohmic voltage drops. The KF–AlF₃–Al₂O₃ system (often referred to as potassium cryolite-based electrolyte) is a leading candidate for low-temperature aluminum electrolysis, specifically aimed at enabling the use of inert anodes.

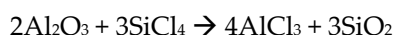
3.2.3. Ionic Liquid for Electrolysis

Recent research explores ionic liquids (ILs) as potential media for direct reduction [102–108] while promising, significant R&D investment is required before commercial viability. Ionic liquids are gaining significant research attention as a “green” alternative to the traditional high-temperature Hall–Héroult process for aluminum electrolysis. Unlike conventional molten salts that require temperatures above 950 °C, ionic liquids allow for the electrodeposition of aluminum at room temperature or below 150 °C, which can theoretically reduce energy consumption by approximately 10.7% to 30%. These electrolytes

offer a wide electrochemical window and high thermal stability, enabling the production of high-purity aluminum with no greenhouse gas emissions like CO₂ or toxic HF. However, the moisture sensitivity of standard chloroaluminate-based ILs remains as a significant industrial barrier, necessitating expensive anhydrous handling and increasing production complexity.

Regarding the raw material costs, it is a valid and primary challenge for large-scale adoption. High-cost precursors such as the established imidazolium-based ionic liquids (e.g., [EMIm]Cl) are prohibitively expensive for commodity-scale aluminum production. The use of cheap raw materials like urea, guanidine, or alkylamine hydrochlorides suffers trade-offs performance. High viscosity and lower ionic conductivity of these cheap alternatives can hinder current efficiency compared to their expensive imidazolium counterparts.

A significant technical challenge in the ionic liquid pathway is the chemical transition from the oxygen-based byproducts (Al(OH)₃ or Al₂O₃) to the chloride-based electrolytes (AlCl₃) required for electrolysis. To achieve this without introducing a carbon footprint, this study proposes an intermediate carbon-free chlorination step utilizing silicon tetrachloride (SiCl₄) as a reagent. SiCl₄ is a high-volume industrial byproduct of the polysilicon industry, and its reaction with alumina:



produces the necessary AlCl₃ while generating high-purity silica as a valuable byproduct. This industrial symbiosis ensures the ionic liquid route remains a strictly carbon-free closed-loop system, avoiding even biogenic CO₂ emissions.

3.3. Integration with Renewable Energy

The carbon intensity of aluminum recycling and aluminum-based energy cycles is determined almost entirely by the source of electricity used for electrochemical processing. When powered by renewable energy, the aluminum–hydrogen cycle can approach true carbon neutrality, positioning aluminum as both a recyclable material and an energy carrier. One pathway is grid-connected renewable integration, in which aluminum production or recycling systems operate flexibly to absorb surplus electricity from solar and wind during periods of overgeneration. In this mode, aluminum electrolysis functions as a form of “virtual battery,” providing demand response, load balancing, and frequency regulation services while converting intermittent renewable electricity into storable chemical energy. However, due to the 7/24 non-stop requirement for a smelter, hydro-powered would be a better choice.

A pathway involves dedicated renewable installations, where aluminum smelters are co-located with large-scale renewable power sources. This model has been successfully demonstrated for decades in hydro-powered smelters in Norway, Iceland, and Canada, where more than 90–95% of electricity originates from renewable hydropower, and is now emerging in regions such as Australia and the Middle East using large-scale solar and wind resources [109–114].

An increasingly attractive approach is the development of hybrid systems that integrate thermal energy storage with renewable electricity, particularly using concentrated solar power (CSP) [115–119]. In such systems, high-temperature solar heat can be directly utilized for thermally intensive steps such as calcination, while renewable electricity supplies the electrochemical reduction stage, enabling higher overall system efficiency and deeper decarbonization of aluminum recycling and production processes.

Case Study: 100% solar-powered aluminum–hydrogen cycle

A 2020 study by Haller et al. [21] modeled a complete system for seasonal energy storage using aluminum. The authors address the critical challenge of the seasonal energy mismatch in cold and moderate climates, the surplus of solar energy in summer versus

the high demand for space heating and electricity in winter. They proposed using an aluminum redox cycle as a compact, high-density seasonal energy storage medium. Aluminum is highlighted for its exceptional volumetric energy density (23.5 MWh/m^3), which is double that of heating oil and significantly higher than hydrogen or lithium-ion batteries. The proposed system operates on a closed-loop material cycle: 1. Charging (Power-to-Al): Excess solar electricity in summer is used to regenerate aluminum from aluminum oxide or hydroxide via electrolysis. 2. Discharging (Al-to-Energy): In winter, the stored aluminum reacts with water to produce hydrogen and heat. 3. Conversion: Hydrogen is fed into a fuel cell to produce electricity, while the heat from both the chemical reaction and the fuel cell is used for domestic hot water and space heating. To achieve 100% solar self-sufficiency, approximately 350–530 kg of aluminum is required per apartment annually.

The review emphasizes that the environmental benefits are largely contingent on moving away from the traditional Hall–Héroult process. As noted in the text, the switch from carbon anodes (producing CO_2) to inert anodes (producing O_2) is what transforms aluminum from a carbon-intensive commodity into a green energy carrier. While the “discharging” phase is suitable for residential basements, the “charging” phase (smelting) requires industrial-scale facilities due to high operating temperatures ($700\text{--}1000^\circ\text{C}$). This necessitates a robust “Al-service” infrastructure like the modern heating oil delivery, which introduces logistical complexity and transport-related emissions, though the study finds these impacts manageable within a 100 km radius.

3.4. Operational Dispatch and System Scheduling

To transition from a technically mature material cycle to a viable energy system, we propose an AI-driven dispatch strategy that treats the aluminum smelter as a flexible grid load. A primary operational challenge in non-continuous smelting is the “thermal start-up penalty” associated with heat loss during inactive periods. However, our analysis demonstrates that this can be effectively managed through dynamic scheduling and low-current idling. The optimization algorithm evaluates a primary decision variable: the Critical Price Threshold. When renewable availability is low or grid prices exceed this threshold, the AI controller reduces the smelter’s power to a standby level sufficient only to maintain the electrolyte in a molten state ($700\text{--}800^\circ\text{C}$ for KF-AlF_3 systems). Simultaneously, the aluminum–water reactor is engaged to provide high-grade exothermic heat (4.4 kWh/kg) to assist in the furnace’s thermal maintenance. This integrated dispatch strategy ensures the system remains “thermally alive” while prioritizing the harvest of zero-cost surplus energy during peak solar windows.

Case Study: 10 MW solar-integrated system

To evaluate the operational viability, we modeled a system powered by a 10 MW solar array (approx. 20,000 panels across 10 hectares). During a 4 h solar peak, the system harvests 40,000 kWh, yielding a gross production of approximately 2666 kg of aluminum (assuming 15 kWh/kg efficiency). To maintain the smelter ‘alive’ at 700°C during the subsequent 20 h standby period, the system consumes 758 kg of Al (approx. 28.4% of daily output) to generate 2000 kWh of thermal maintenance heat. The remaining 1908 kg of net aluminum represents the harvested energy available for seasonal storage, demonstrating that the system can sustain continuous industrial operation even under intermittent renewable supply. Comparison with a traditional 24/7 mode and the AI-driven mode is shown in Table 1.

Table 1. Operational and infrastructure metrics for a 10 MW integrated system.

Operational Metric	Traditional 24/7 Industrial Mode	AI-Driven Dispatch Mode (10 MW Scale)	Strategic Advantage/Disadvantage
Renewable Integration Rate	30–40%	>85%	Maximizes use of peak surplus solar energy.
Infrastructure Scale	Dependent on stable grid power.	20,000 Solar Panels (~10 Hectares)	Ideal for off-grid and remote applications./High initial CAPEX for 10MW
Daily Energy Harvest	Fixed low-output production.	40,000 kWh (4 h Burst Production)	High-intensity production during peak sun hours.
Gross Aluminum Output	Not optimized for intermittency.	~2666 kg Al/day	Achieved at an efficiency of 15 kWh/kg.
Thermal Strategy	Constant external heating.	Reaction Heat Recovery (758 kg Al/day)	Uses 28.4% of output for 20 h maintenance.
Daily Net Energy Yield	Vulnerable to price volatility.	~1908 kg Net Aluminum/day	High energy surplus after all maintenance costs.
System Role	Passive grid consumer.	Active Virtual Battery	Provides grid-balancing and peak-shaving./Logistical complexity of solid byproduct recovery

4. Energy Efficiency Analysis

The “Green Aluminum” energy cycle represents a promising closed-loop system for carbon-neutral energy storage and transport. The following analyzes the energy efficiency of a specific cycle: the reaction of aluminum powder with water to generate hydrogen and heat, followed by the recovery of aluminum via low-temperature electrolysis (700 °C) using inert anodes. It aims for commercial pilot deployment within 5–10 years, acknowledging significant engineering hurdles in cell longevity and scale-up.

4.1. Step-by-Step Energy Balance

Take 1 kg aluminum powder for discussion.

Step 1: Aluminum–water reaction (energy discharge). In this stage, 1 kg of Al powder reacts with water. This process is the primary “power generation” phase of the cycle. Reaction (1) will be carried out. It will produce 0.111 kg of H₂, if we assume this is at a Lower Heating Value (LHV) of 33.3 kWh/kg, this yields 3.7 kWh. At the same time, the exothermic nature of the reaction releases approximately 4.4 kWh of thermal energy. If hydrogen is used through fuel cells (50–60%), then the energy is only 2.04 ± 0.19 kWh output as electricity.

Step 2: Calcination of byproducts. In this stage, the resulting Al(OH)₃, around 2.889 kg, is calcined to produce 1.889 kg Al₂O₃. Theoretically, the required energy is ~0.95 kWh/kg Al. Including industrial thermal losses, we assume 1.1 kWh/kg Al for this analysis.

Step 3: Low-temperature smelting. The Al₂O₃ is reduced in a KF–AlF₃ eutectic melt at 700 °C. The electrolytic reduction using inert anodes to eliminate CO₂ emissions. Operating at 700 °C significantly reduces thermal maintenance energy compared to standard 960 °C cells. It is estimated to be 12.5 kWh/kg Al.

Step 4: Atomization. To complete the cycle, liquid aluminum is processed through an Argon (Ar) high-pressure nozzle to become powders. Energy is assumed to be ~0.2 kWh/kg Al (mechanical/compression). In this process, since liquid aluminum droplets need to be cooled to room temperature into powders, the exhaust thermal energy can be collected, with appropriate system integration.

Therefore, we end up with a total input (recharge) of 13.8 kWh (smelting + calcination + atomization) and a total output (discharge) of 8.1 kWh (hydrogen + recoverable Heat) or

6.6 kWh (electricity + recoverable heat). We could tabulate all these estimates for clarity, as shown in Table 2.

Table 2. Practical efficiency summary.

Charge/Discharge as	Hydrogen	Electricity (via Fuel Cells)
Total input energy (Recharge)	13.8 kWh	13.8 kWh
Hydrogen energy output (LHV)	3.7 kWh	2.04 ± 0.19 kWh
Recovered reaction heat ($60 \pm 10\%$)	2.64 ± 0.44 kWh	2.64 ± 0.44 kWh
Recovered cooling heat ($30 \pm 5\%$)	0.09 ± 0.01 kWh	0.09 ± 0.01 kWh
Round-trip efficiency	$46.6 \pm 3.3\%$	$34.5 \pm 4.6\%$

Remarks:

1. The Lower Heating Value (LHV) of hydrogen is approximately 120 MJ/kg or 33.3 kWh/kg. This is the energy released when hydrogen is burned and the resulting water remains as vapor.
2. By replacing carbon with inert anodes, we produce pure O₂ instead of CO₂, removing 1.5 kg of carbon emissions per kg of metal.

The KF-AlF₃ system at 700 °C allows for less-expensive vessel materials and significantly lower radiant heat loss, improving overall voltage efficiency. The green aluminum energy cycle provides a robust alternative to liquid fuels. While 34.5–46.6% energy round-trip efficiency is moderate, the ability to recover high-grade heat during the water reaction elevates the system to even higher efficiency, making it an ideal candidate for industrial seasonal energy storage. However, efficiency will be 14.8–26.8% if the thermal energy is not recovered.

The relatively high round-trip energy efficiencies (36–47%) estimated for the aluminum–hydrogen–electricity pathway represent an upper-bound, component-level performance that is achievable only under system configurations in which continuous low-carbon electricity is available beyond the limited high-solar window. In regions where solar irradiation is confined to a few hours per day (e.g., ~4 h), maintaining uninterrupted aluminum production and realizing high utilization of recovered reaction heat require integration with complementary renewable or firm low-carbon power sources, such as hydro-power, wind, or grid-supplied electricity during the remaining low-sunlight period (~20 h). Under such hybrid renewable systems, aluminum reduction can proceed without interruption. Consequently, the system-level efficiency of aluminum-based energy storage is strongly dependent on the availability of complementary renewable power, and the reported efficiencies should be interpreted as conditional values applicable to integrated, multi-source renewable energy systems rather than a standalone solar-only operation.

4.2. Comparison with Alternative Energy Storage Technologies

To understand the viability of the green aluminum cycle, it must be compared against established energy storage systems. While electrochemical batteries excel in short-term efficiency, the Al-H₂ cycle offers a paradigm shift in energy density and storage duration.

4.2.1. Technical Performance Benchmarking

The following Table 3 compares the Al-H₂ cycle with leading storage technologies across three critical metrics: round-trip efficiency (RTE), volumetric energy density, and typical storage duration.

Table 3. Comparison of energy storage technologies.

Technology	Round-Trip Efficiency (%)	Energy Density (Wh/L)	Typical Duration
Lithium-ion Battery	85–95%	200–400	Hours to Days
Vanadium Flow Battery (VFB)	65–75%	20–40	Hours to Weeks
Pumped Hydro Storage	70–85%	0.5–1.5	Hours to Months
Compressed Air Energy Storage (CAES)	40–55%	2–6	Hours to Days
Compressed Hydrogen (700 bar)	30–45%	1000–1500	Days to Months
Aluminum–Hydrogen Cycle	36–47%	23,500	Weeks to Seasons

Key comparative insights:

1. The “energy density” champion: The Al-H₂ cycle’s density (23,500 Wh/L) is roughly 15 to 20 times higher than compressed hydrogen and 60 to 100 times higher than lithium-ion batteries. This makes it the only viable “green” option for space-constrained industrial sites or heavy-duty mobile platforms. At the system level, including the Al–water reactor, dehumidifiers, and balance-of-plant components, the effective volumetric energy density is estimated to be 40–60% lower, though still significantly higher than compressed hydrogen systems.
2. Efficiency vs. duration trade-off: While batteries have a much higher efficiency (>90%), they suffer from “self-discharge” and high costs for large capacities. Aluminum acts as a “solid fuel” with zero self-discharge, meaning you can store solar energy in the summer and use it for heating in the winter with no loss of the “fuel” itself.
3. Safety and stability: Unlike high-pressure hydrogen (700 bar) or volatile battery chemistries, aluminum is a stable solid. It is non-toxic, non-explosive in bulk form, and can be transported using existing global shipping infrastructure.

4.2.2. Economic Comparison of Hydrogen Production

A major hurdle for the Al-H₂ cycle is the current cost of production compared to traditional and emerging methods. Below, Table 4 is a cost-per-kilogram breakdown of hydrogen generation. The projected ‘Optimized’ cost of 6.00–12.00 USD/kg H₂ is derived from a techno-economic model that assumes large-scale adoption of inert anode technology. A representative cost breakdown includes the following:

Energy input (13.8 kWh @ 0.04 USD/kWh): 0.55 USD /kg Al (approx. 5.00 USD/kg H₂).

Capital and operational expenses (smelter/reactor): 2.50–4.50 USD/kg H₂.

Feedstock logistics (byproduct transport): 1.00–2.00 USD/kg H₂.

Byproduct credits (O₂ sale and carbon credits): (–2.50 to –3.00 USD/kg H₂).

This structure demonstrates that the competitiveness of the Al-H₂ cycle is heavily contingent on high-utilization rates and the valorization of industrial byproducts.

Table 4. Cost per kg hydrogen generation.

Production Method	Current (USD/kg H ₂)	Projected 2030 (USD/kg H ₂)	CO ₂ Intensity
Natural Gas (SMR)	1.00–2.50	1.50–2.00	High
Renewable Electrolysis	5.00–8.00	2.50–4.00	Zero
Al-H ₂ (Current)	15.00–25.00	10.00–18.00	Zero *
Al-H ₂ (Optimized)	—	6.00–12.00	Zero *

* Assumes the aluminum smelting process is powered by renewable electricity with inert anodes.

Why is Al-H₂ more expensive?

- Infrastructure: Electrolysis creates H₂ directly from water. The Al-H₂ cycle requires an intermediate step (smelting Al), which adds capital and energy costs.

- The “offset” strategy: To make the cycle competitive, the byproduct $\text{Al}(\text{OH})_3$ must be recycled efficiently. Currently, recycling offsets approximately USD 2.70 to USD 5.40 per kg of H_2 produced, which is already factored into the “Optimized” projections.
- While the Al- H_2 cycle offers superior storage stability, it suffers from significant round-trip energy losses and high capital expenditure (CAPEX) for integrated smelting and powder-atomization facilities. Furthermore, the logistical requirement to transport mass-equivalent amounts of $\text{Al}(\text{OH})_3$ back to recycling centers introduces a complexity not found in decentralized water electrolysis.

4.2.3. The Multi-Criteria Verdict

When choosing a storage technology, the “best” option depends on the application:

- Short-term grid balancing: Lithium-ion is superior due to high round-trip-efficiency.
- Geographic specifics: Pumped hydro is best if you have mountains and water.
- Seasonal and industrial energy: The aluminum–hydrogen cycle is the frontrunner because it allows for the massive, stable storage of energy that can be “discharged” as both hydrogen and high-grade heat ($>60\text{ }^\circ\text{C}$) exactly when and where it is needed.

Efficiency is not the only factor; safety, scalability, and geographic limitations often dictate which technology is deployed. Table 5 compares the safety, geographic constraints, scalability, self-discharge, and technology readiness level among Al- H_2 cycle and other methods.

Table 5. Strategic comparison matrix (qualitative factors).

Criterion	Al- H_2 Cycle	Li-Ion Battery	Pumped Hydro	Compressed H_2
Safety	High (Solid)	Medium (Thermal)	High	Medium (Pressure)
Geographic Constraints	Low	Low	High (Mountains)	Low
Scalability	High	High	Limited by site	High
Self-Discharge	0%/month	1–5%/month	0%	0.5–1%/month
Tech Maturity (TRL)	4–6	9	9	8

4.3. Technical Challenges

Despite significant progress, five technical barriers must be overcome for commercial deployment. First, Passivation Management is critical for sustained reaction rates; solutions include using recyclable organic activators (like imidazole), developing self-activating ternary alloys or nano-sized $\text{Al}(\text{OH})_3$, or employing dynamic methods (ultrasonic/mechanical) to continuously disrupt the blocking oxide layer. However, it is essential to distinguish between laboratory proof-of-concept and industrial scalability; while Ga-In alloys are effective, mechanical milling (ball milling) and self-activating ternary alloys are currently the most viable for large-scale industrial use due to easier handling and lower cost compared to high-purity liquid metal coatings (Ga-In).

Second, reactor scale-up requires transitioning from the lab to industrial scale while handling intense exothermic heat. Strategies involve modular reactor arrays for distributed production and “heat integration” systems that capture waste heat for desalination or district heating. Third, Direct Electrolytic Reduction—converting $\text{Al}(\text{OH})_3$ back to aluminum without energy-intensive calcination—remains an early-stage challenge. Research is currently focused on ionic liquids and low-temperature molten salts to bypass traditional high-heat methods. Finally, System integration relies on “digital twins” to optimize energy flows and geographic co-location, ensuring that aluminum production aligns perfectly with renewable energy availability and logistics.

Fifth, the development of robust inert anodes remains a primary bottleneck for transitioning to the green Hall–Héroult process. Current advanced materials, such as nickel

ferrite-based cermets and specialized metallic alloys, are currently at a Technical Readiness Level (TRL) of 4–6, with successful demonstrations limited to laboratory and small-scale pilot cells. The fundamental challenge resides in long-term durability; the aggressive nature of molten fluoride salts, combined with the continuous evolution of pure oxygen, can lead to slow chemical dissolution or mechanical degradation of the anode over time. Achieving the multi-year operational lifespan required for industrial competitiveness necessitates further breakthroughs in material stability and the formation of self-healing protective oxide scales during high-temperature electrolysis.

4.4. Environmental Sustainability

When optimized with renewable energy and recycling, the aluminum–hydrogen cycle achieves a carbon footprint as low as 1.0–2.0 kg CO₂ per kg H₂, making it competitive with direct green electrolysis. The system benefits from aluminum’s established recycling infrastructure, capable of >95% material recovery in a closed loop—vastly outperforming the 5–10% recycling rates of lithium-ion batteries. Water management is also flexible; while the process consumes ~20–40 kg of water per kg of hydrogen, its ability to utilize seawater makes it viable even in arid regions. Ultimately, this cycle significantly reduces the ecological impact of bauxite mining and eliminates direct emissions, if challenges regarding activator toxicity and industrial safety are effectively managed. When powered by renewable energy, the aluminum–hydrogen cycle offers substantial environmental benefits compared to fossil-based alternatives, with sustainability performance approaching that of direct renewable electrolysis.

A structured comparison table highlighting how it outperforms or matches competing technologies is shown in Table 6.

Table 6. Comparison of key metrics of Al-H₂ cycle to other energy storage methods.

Metric	Optimized Al-H ₂ Cycle	Current Industry Standard/Competitor	Key Advantage
Carbon Footprint	1.0–2.0 kg CO ₂ /kg H ₂	9–12 kg CO ₂ (Gray Hydrogen)	Genuine “green” status: Matches the low emissions of direct water electrolysis (0.5–2 kg CO ₂).
Material Recycling	>95% Recovery Rate	5–10% (Lithium-Ion Batteries)	True circularity: Aluminum has a mature infrastructure, unlike the <1% recycling rate for rare earth magnets.
Water Usage	Seawater Compatible	Freshwater Required (Electrolysis)	Geographic flexibility: Can operate in arid regions by using saltwater, unlike standard electrolysis which relies on purified water.
Mining Impact	Reduced (Closed-Loop)	High (Continuous Extraction)	Resource independence: High recycling rates drastically lower the need for new Bauxite mining, protecting local ecosystems.
System Efficiency	0.95+ Circularity Index	Linear Consumption (Fossil Fuels)	Minimal waste: Material losses are kept to <5% per cycle.

4.5. Application-Specific Suitability

The aluminum–hydrogen cycle is uniquely suited for applications requiring high energy density and long-term stability, areas where conventional batteries often face limitations. Its primary strength lies in seasonal energy storage, offering a mechanism to shift summer solar surpluses to meet winter heating demands or agricultural cycles (harvest to planting). Beyond grid balancing, the technology is ideal for off-grid and remote power, providing safe, portable energy for island communities, remote mining operations, and disaster relief efforts without the need for complex grid infrastructure. In the transportation sector, it serves as a viable solid fuel for maritime shipping and long-haul trucking, effectively bypassing the logistical hazards of compressed hydrogen infrastructure.

Furthermore, it enables decentralized industrial hydrogen supply, allowing manufacturing facilities (e.g., ammonia, steel, refining) to generate hydrogen on-site and on-demand, eliminating the costs and risks associated with hydrogen transport.

Despite its advantages, the technology is less suitable for short-duration grid storage (1–4 h) or applications requiring frequent daily cycling. In these scenarios, lithium-ion batteries offer superior round-trip efficiency and faster response times. Additionally, while the energy density of aluminum is high, the absolute weight of the required reaction systems may limit its feasibility in highly weight-sensitive applications, such as small-scale aerospace.

Rather than competing directly with established storage technologies, the aluminum–hydrogen cycle is best implemented within hybrid systems that leverage the strengths of multiple technologies:

- Battery + aluminum (short- and long-duration): A tiered storage approach where batteries handle daily load variations with high efficiency, while aluminum reserves are utilized for long-term, seasonal storage, optimizing overall system cost and performance.
- Electrolysis + aluminum (dual pathway): A flexible production model where direct water electrolysis meets immediate hydrogen demand, while aluminum production is engaged during periods of surplus renewable energy to store excess power as solid fuel.
- Pumped hydro + aluminum (geographic complementarity): A spatial strategy where pumped hydro is deployed in topographically suitable regions, while aluminum systems are installed in flat or dense urban areas, ensuring comprehensive regional energy coverage.

5. Conclusions

This review confirms that a closed-loop aluminum–hydrogen system is technically mature for hydrogen production, achieving 85–98% of theoretical yields under optimized conditions. While the system’s round-trip efficiency (34.5–46.6%) is lower than batteries (85–95%) or pumped hydro, it is comparable to compressed air storage and ideal for long-duration applications where other options are too expensive. However, economics remain the primary hurdle: current costs are 15–25 USD/kg H₂, significantly higher than renewable electrolysis (5–8 USD/kg).

Economic viability hinges on commercializing the inert anode, green Hall–Héroult process and skipping the calcination process. Unlike traditional smelting, which faces high consumable costs for carbon anodes, this advanced method utilizes durable inert anodes to eliminate anode replacement expenses and generates high-purity oxygen as a marketable byproduct. Furthermore, the integration of wettable cathodes allows for reduced inter-electrode spacing, significantly lowering resistive energy losses. Elimination of the calcination process of Al(OH)₃ by using a high-pressure reactor for Al–water reaction, where Al₂O₃ together with hydrogen is the byproduct. By “stacking” revenues from industrial oxygen sales and carbon credits—while capitalizing on the operational efficiency of inert anode cells and skipping the calcination process—the effective production cost can be driven down.

When powered by renewable energy, this cycle is genuinely green. It achieves a carbon footprint of 1–2 kg CO₂-eq/kg H₂, matching direct water electrolysis, whereas fossil-powered aluminum production yields an unsustainable 108–144 kg CO₂-eq/kg H₂. The system also excels in resource efficiency, offering >95% material recyclability—far superior to the 5–10% recycling rates of lithium-ion batteries—and offering flexibility in water sourcing, including the use of seawater.

Technically, the industry must transition from the standard Hall–Héroult process (~50% efficiency) to a lower-melting salt electrolytic reduction (potential ~60% efficiency) and solve reactor scale-up challenges. Economically, the high upfront capital for

integrated facilities and the current 3–5× cost premium over electrolysis deter investment. Politically, the technology lacks specific support; most green hydrogen incentives target electrolysis, and safety standards for aluminum-based systems are currently undefined.

Although aluminum–water reactions enable on-demand hydrogen generation and allow renewable electricity to be stored in a stable solid form, the aluminum–hydrogen pathway should not be interpreted as a high-efficiency closed-loop energy recycling system. The electrical energy required for aluminum reduction significantly exceeds the recoverable electricity obtained from subsequent aluminum oxidation, and when daily solar availability is limited (e.g., ~4 h), reliance on aluminum-derived electricity to sustain continuous aluminum smelting would require impractically large renewable overcapacity or supplementary firm power sources. Consequently, aluminum cannot function as a daily charge–discharge buffer for its own production. Instead, continuous smelting must be supported by direct and firm low-carbon electricity (e.g., wind, hydro, nuclear, ocean wave, or grid supply), while aluminum produced during periods of surplus renewable availability serves as a long-duration, loss-free chemical energy carrier. In this role, aluminum enables the temporal and spatial decoupling of renewable electricity generation from hydrogen demand, particularly for seasonal storage, remote energy transport, or applications where hydrogen infrastructure is impractical. Under these conditions, the aluminum–hydrogen system is best viewed not as an alternative to batteries or direct electrification, but as a complementary pathway for valorizing otherwise-curtailed renewable energy and providing dispatchable hydrogen and heat with high storage stability. Ultimately, the transition from a technically mature material cycle to a viable energy system requires the integration of dispatch optimization and digital twin monitoring. When placed within the context of a global renewable supply chain, the aluminum–H₂ system acts as a dispatchable long-duration energy buffer, providing a resilient, zero-carbon alternative to traditional fuel infrastructures.

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