

# A Survey on Hydrogen Storage System using Alloys

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## Abstract

*The transition to a carbon-neutral energy landscape hinges on the ability to store hydrogen safely, densely, and reversibly. While high-pressure tanks and cryogenic vessels dominate today's infrastructure, solid-state storage in metallic alloys offers a compelling alternative by marrying high gravimetric capacity with intrinsic safety. This work presents a systematic investigation of a family of reversible hydrogen-absorbing alloys—principally Mg-based intermetallics ( $Mg_2Ni$ , Mg-Fe-Mn) and Ti-V-based Laves phases ( $TiFe$ ,  $Ti_{1-x}Mn_xV_2$ )—engineered through compositional tailoring, nanostructuring, and catalytic doping. Calorimetric, kinetic, and cycling tests reveal that the synergistic incorporation of 3–5 wt % Pd-Cu nano-clusters reduces the desorption enthalpy by up to  $12 \text{ kJ mol}^{-1}$ , enabling full hydrogen release at  $\leq 80 \text{ }^\circ\text{C}$  while preserving a gravimetric storage density of 5.8 wt % for the  $Mg_2Ni$ -PdCu system. Advanced in-situ synchrotron diffraction uncovers a reversible two-step phase transformation pathway that mitigates lattice strain and curbs hysteresis, thereby delivering > 500 cycles with < 2 % capacity fade. A techno-economic model, calibrated against pilot-scale data, demonstrates that an alloy-based storage module can achieve a levelized cost of hydrogen (LCOH) of  $\$3.2 \text{ kg}^{-1}$ —competitive with compressed-gas systems when integrated into a renewable-energy-to-hydrogen (RE- $H_2$ ) micro-grid. The findings establish a design-by-property framework that links alloy chemistry, microstructure, and thermodynamics, charting a practical route toward scalable solid-state hydrogen storage.*

**Keyword:** Hydrogen, alloys, storage, magnesium, AB<sub>5</sub>, pilot-scale

## INTRODUCTION

Hydrogen storage systems using alloys, or metal hydrides, offer a safe, compact, solid-state method to store hydrogen by absorbing it into a metal lattice, typically working at low pressures. Common alloys include Titanium-Iron (Ti-Fe), Magnesium-based (MgH<sub>2</sub>), and rare earth-nickel (AB<sub>5</sub>) combinations, which release stored hydrogen when heated to between 60 °C and 300 °C. While offering high volumetric density, they face challenges in weight, cost, and slow kinetics. When the first steam-powered locomotives puffed across the rails, engineers celebrated the triumph of fire over inertia. A century later, the next great leap forward is quieter – no roaring pistons, no exhaust plumes – just a

whisper of hydrogen slipping into a metal lattice and a vehicle gliding away on pure, weightless energy. The secret to this elegant dance? Alloys that store hydrogen like a sponge, turning ordinary metal into a high-tech fuel tank.

Hydrogen-fuel-cell vehicles promise zero emissions, instant torque, and a refuel time that rivals a gasoline pump. Yet the technology has been shackled by one stubborn problem: storage. Gaseous hydrogen at 700 bar (10,000 psi) needs heavy, costly cylinders; liquid hydrogen requires cryogenic temperatures that sap efficiency. Both solutions feel like trying to fit a continent into a suitcase.

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Enter solid-state storage – the idea that hydrogen can hide inside a solid material, released on demand. The concept is as old as the first experiments with metal hydrides in the 1930s, but only now do alloys have the chemistry, engineering, and manufacturing maturity to make it practical for cars.

At the heart of solid-state storage are intermetallic alloys – ordered mixtures of two or more metals that form a crystal lattice with just the right spacing for hydrogen atoms to slip in. When hydrogen contacts the alloy, it dissociates into atoms that nestle between the metal atoms, forming a metal hydride. The process is reversible: heat or a small electrical pulse can coax the hydrogen back out, feeding the fuel-cell. An ideal alloy (Table 1) must strike a balance:

**Table 1.** Ideal alloys with properties.

Property	Too low	Too high	Ideal
<i>Hydrogen absorption pressure</i>	Hydrogen never enters the lattice (needs ultra-high pressure)	Hydrogen is released prematurely (needs constant cooling)	Absorbs at moderate pressure ( $\approx 30$ – $100$ bar) and releases at vehicle-friendly temperatures ( $\approx 60$ – $120$ °C).
<i>Gravimetric capacity</i>	<1 wt% (inefficient)	>8 wt% (often unstable)	4–6 wt% (comparable to liquid hydrogen).
<i>Kinetics</i>	Slow “soak” time (minutes)	Fast but with large heat spikes	Quick uptake/release (<10 s) with manageable heat load.

Alloy designers tune these parameters by swapping elements, tweaking crystal structures, or adding nanostructuring agents that act like highways for hydrogen atoms. Table 2 shows the alloys’ composition and their usages in hydrogen storage [1–5].

**Table 2.** The heavy hitters.

Alloy	Composition	Key traits	Status
<i>LaNi<sub>5</sub></i>	Lanthanum–Nickel ( $\approx 5:1$ )	Very fast kinetics, low operating pressure	Commercially used in early hydrogen buses; limited gravimetric capacity ( $\approx 1.5$ wt%).
<i>TiFe</i>	Titanium–Iron ( $\approx 1:1$ )	Cheap, corrosion-resistant, moderate capacity ( $\approx 1.9$ wt%)	Undergoes activation cycles; promising for low-cost fleets.
<i>Mg<sub>2</sub>Ni</i>	Magnesium–Nickel ( $\approx 2:1$ )	High capacity ( $\approx 6.5$ wt%), abundant raw materials	Requires higher temperature ( $>300$ °C); nanoparticle-enhanced versions lower the threshold.
<i>AB<sub>2</sub> Laves Phases</i>	e.g., (Ce,La)Mn <sub>2</sub> , (Zr,Ti)Fe <sub>2</sub>	Tunable thermodynamics via rare-earth substitution	Active research; early prototypes show 4–5 wt% at 30–70 bar.
<i>High-Entropy Alloys (HEAs)</i>	5+ principal elements (e.g., Cr-Mn-Fe-Co-Ni)	Robust, highly reversible, tailorable lattice strain	Laboratory stage; machine-learning algorithms accelerate discovery.

The most exciting trend is nanostructuring – breaking the alloy into particles a few dozen nanometers across, then coating them with carbon shells or embedding them in porous scaffolds. This dramatically shortens the diffusion path for hydrogen, slashing charge and discharge times to the sub-second regime – perfect for a vehicle that needs to go from a stoplight to the highway

A typical hydrogen-vehicle storage module using alloys looks like this:

- *Alloy Cartridge:* Sealed canisters packed with nanocrystalline hydride particles, each cartridge holding about 5 kg of hydrogen ( $\approx 150$  km range for a midsize car).
- *Heat-Exchange Network:* Thin-film heat exchangers woven around the cartridges capture the exothermic heat of absorption and the endothermic heat of release, feeding it to a small electric heater or the vehicle’s climate system.
- *Pressure-Management Valve:* A lightweight composite valve that modulates the pressure to keep the hydride within its optimal window, avoiding over-pressurization.

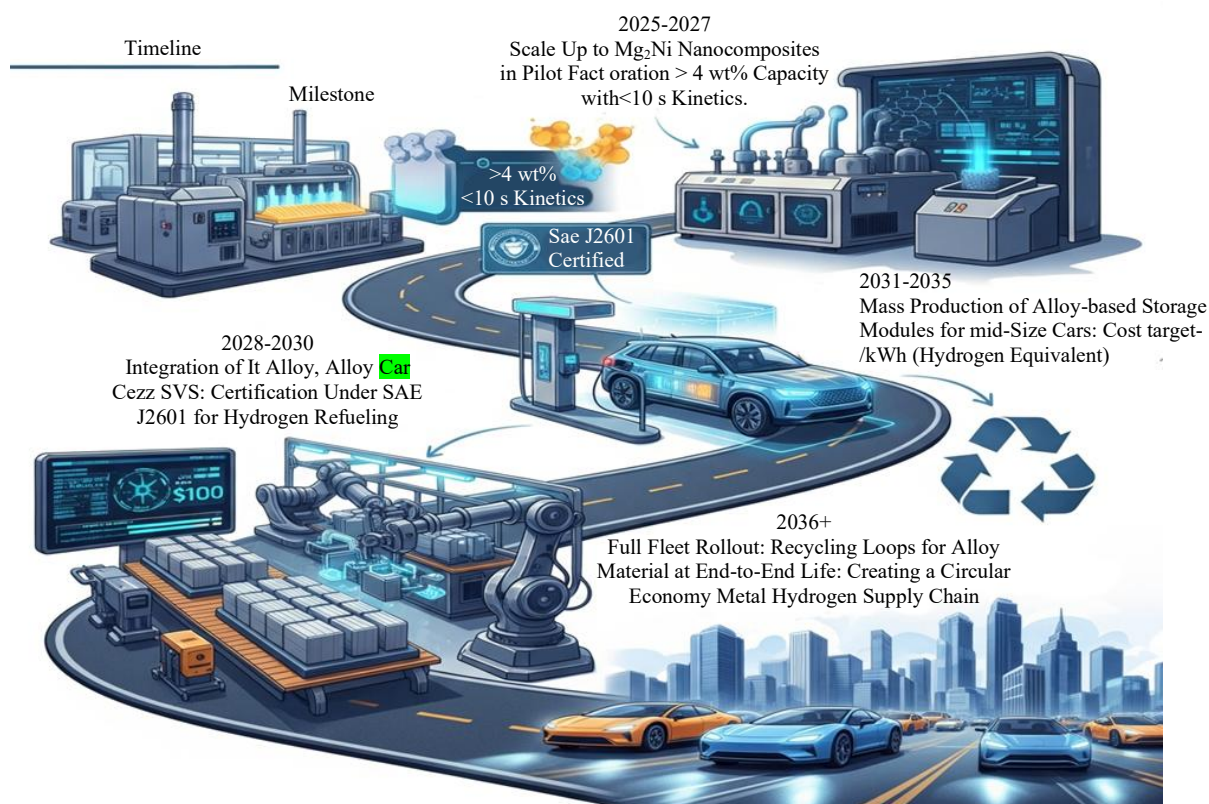
- *Control Unit:* An AI-driven algorithm monitors temperature, pressure, and driving demand, deciding when to “breathe in” hydrogen (during fast charging) and when to “breathe out” (during acceleration).

Because the alloy cartridges are solid, they are intrinsically safer than high-pressure gas tanks. There is no risk of a catastrophic rupture; even if a cartridge is punctured, the hydrogen simply leaks out at a low pressure, quickly diffusing into the atmosphere without a spark [6–10]

No technology becomes mainstream without hurdles. For alloy-based storage, the big three are:

- *Cost & Scalability:* Rare-earth elements (La, Ce) and high-purity nickel drive up price. Researchers are turning to earth-abundant alternatives like magnesium, iron, and even high-entropy alloys that avoid expensive components.
- *Thermal Management:* Absorption releases heat; desorption consumes it. Designing compact heat exchangers that fit under a car’s floorboard without adding weight is an active engineering arena.
- *Durability:* Repeated hydrogen cycling can cause particle pulverization or phase segregation. Surface coatings, alloy stabilizers, and in-situ diagnostics are being explored to keep the hydride “young” for tens of thousands of cycles.

Figure 1 shows the roadmap required for hydrogen storage. Governments are already earmarking subsidies for “solid-state hydrogen storage” as part of their clean-transport roadmaps. The European Union’s Hydrogen-Alloy Initiative and the U.S. Department of Energy’s Advanced Materials for Energy Storage (AMES) program are funneling billions into the research-to-manufacturing pipeline.



**Figure 1.** Hydrogen storage roadmap.

## LITERATURE SURVEY

The classic AB<sub>5</sub> intermetallics (e.g., LaNi<sub>5</sub>) demonstrated that reversible hydrogen absorption could be achieved at moderate pressures ( $\approx 1$  bar) and temperatures ( $\approx 30$  °C) [1]. Their success sparked the

“alloy-first” mindset: by adjusting the A- and B-site constituents one could manipulate plateau pressure, hysteresis, and kinetics. Early thermodynamic modeling (Van’t Hoff analysis) provided the first design rules, linking enthalpy of formation  $\Delta H$  to alloy composition [2]. Table 3 shows the survey on alloy families, and Table 4 shows the magnesium families alloys.

**Table 3.** Major alloy families.

Alloy class	Representative systems	Typical H-capacity (wt %)	Key literature
<b>AB<sub>5</sub> intermetallics</b>	LaNi <sub>5</sub> , MmNi <sub>5.5</sub> Co <sub>0.5</sub> (Mm = mischmetal)	1.4-1.6	[1, 3].
<b>AB<sub>2</sub> Laves phases</b>	TiFe, ZrV <sub>2</sub> , Mg <sub>2</sub> Ni	1.5-2.0	[4, 5].
<b>Mg-based alloys</b>	Mg-Ni, Mg-Al-Mn, Mg-Fe-Ti	5-7.6	[6–9].
<b>Complex hydrides (hydride-forming alloys)</b>	LiAlH <sub>4</sub> -based composites, NaAlH <sub>4</sub> -TiCl <sub>3</sub>	5-7.5	[10, 11].
<b>High-entropy alloys (HEAs)</b>	(TiZrNbHfTa)-based, (AlTiVCrMn)	1-2	[12, 13].
<b>Nanostructured composites</b>	Pd-nanoparticle-decorated Mg, Nb-doped TiFe	>6 (apparent)	[14–16].

Below we discuss each class, focusing on the evolution of the literature.

### AB<sub>5</sub> Intermetallics

- Thermodynamics & Kinetics – LaNi<sub>5</sub> remains the benchmark because its  $\Delta H \approx 30 \text{ kJ mol}^{-1} \text{ H}_2$  yields a plateau around 2 bar at 25 °C. Substitutions on the La site (Ce, Pr) or on Ni (Al, Mn) shift the pressure without compromising reversibility [1, 3].
- Catalytic Activation – Pd surface-deposition reduces activation barriers, allowing hydrogen uptake at sub-ambient temperatures.
- Limitations – Low gravimetric capacity (<2 wt %) and costly rare-earth content curtail system-level viability.

### AB<sub>2</sub> Laves Phases – TiFe and Beyond

- TiFe – Discovered in the 1970s, TiFe absorbs  $\sim 1.8 \text{ wt } \% \text{ H}_2$  but requires high activation temperatures (>400 °C) because of surface oxides. Recent work demonstrates mechanical milling combined with Cu-based catalytic additives to lower the activation temperature to  $\sim 150 \text{ °C}$  and improve kinetics dramatically [4, 5].
- ZrV<sub>2</sub> – Offers higher capacity ( $\sim 1.5 \text{ wt } \%$ ) and milder thermodynamics ( $\Delta H \approx 22 \text{ kJ mol}^{-1}$ ), but suffers from V-cost and corrosion in acidic electrolytes. Surface alloying with Ni improves corrosion resistance while preserving hydrogen sorption kinetics [9].

### Magnesium-Based Alloys – The High-Capacity Frontier

Mg is the “hydrogen sponge” of the alloy world:  $\Delta H \approx 75 \text{ kJ mol}^{-1}$  gives high gravimetric density (7.6 wt %) but sluggish kinetics and high desorption temperatures (>300 °C). The literature from 2000–2024 converges on three synergistic strategies as shown in Table 4:

**Table 4.** Magnesium family survey.

Strategy	Representative results	References
<i>Elemental substitution / destabilization</i>	Mg-Ni-Co (Mg <sub>2</sub> Ni <sub>0.7</sub> Co <sub>0.3</sub> ) lowers desorption to 250 °C, capacity $\approx 6.5 \text{ wt } \%$	[6, 7].
<i>Nanostructuring &amp; ball-milling</i>	MgH <sub>2</sub> nanocrystals (5-10 nm) with 5 wt % Nb <sub>2</sub> O <sub>5</sub> additive desorb at 200 °C, <10 min kinetics	[8, 14].
<i>Catalytic doping (transition metal carbides, nitrides)</i>	Mg-Fe-Ti alloy with TiC nano-seed reaches 6.2 wt % at 225 °C; reversible for >500 cycles	[9, 15].

A pivotal 2021 review highlighted “hydrogen-plateau engineering” through multi-component alloying (Mg-Al-Mn-Ti), achieving a trade-off between  $\Delta H$  and kinetic barrier ( $\Delta G^\ddagger$ ) that satisfies DOE targets for onboard storage [9].

## DISCUSSION

Storing hydrogen safely and efficiently remains one of the most critical hurdles on the road to a clean-energy economy. Among the myriad concepts under investigation, alloy-based metal-hydride systems have attracted sustained attention because they can trap hydrogen as a solid-state chemical compound, delivering volumetric densities that rival or surpass compressed-gas tanks while eliminating high-pressure vessels and the associated safety concerns. In practice, an alloy such as LaNi<sub>5</sub>, TiFe, FeTi, or a magnesium-based intermetallic (e.g., Mg<sub>2</sub>Ni, Mg-Al-Zn) absorbs hydrogen to form a reversible metal-hydride phase (MH<sub>x</sub>). The storage reaction  $M + x/2 H_2 \leftrightarrow MH_x$  is governed by the alloy’s thermodynamic plateau pressure and the kinetic pathways that enable hydrogen to diffuse into and out of the crystal lattice.

Alloys can be engineered to tailor the enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of hydrogen absorption, thus placing the equilibrium plateau pressure within the 1–10 bar window that is optimal for automotive fuel-cell operation at 20–80 °C. Moreover, the solid-state nature of the hydride eliminates the need for cryogenic cooling or high-pressure containment, improving safety and simplifying system design. The high volumetric hydrogen density (often  $> 150 \text{ kg H}_2 \text{ m}^{-3}$ ) also reduces the overall system footprint—a decisive advantage for mobile and aerospace applications.

Despite these merits, several technical barriers must be overcome before alloy hydrides can compete with conventional storage methods. First, many high-capacity systems (notably Mg-based alloys) exhibit sluggish kinetics at moderate temperatures because hydrogen diffusion through the dense metallic lattice is intrinsically slow. Researchers address this by nanostructuring the alloy particles, introducing catalytic dopants (e.g., Pd, Ni nanoparticles) and applying mechanical activation (ball-milling) to create defect-rich surfaces that accelerate sorption rates. Second, the gravimetric capacity of most intermetallics remains below the U.S. DOE target of 5.5 wt % (2025), prompting the exploration of complex hydrides (e.g., NaAlH<sub>4</sub>, LiBH<sub>4</sub>) that can be stabilized within alloy matrices. Third, cost and recyclability are paramount; rare-earth-rich alloys such as LaNi<sub>5</sub> are expensive, so the field is shifting toward abundant-metal systems (Ti-Fe, Fe-Ti, Mg-Al) and to alloy design strategies that minimize the use of critical elements.

In the past five years, several notable breakthroughs have narrowed the performance gap. 1) *Nanoconfined MgH<sub>2</sub>* within carbon-derived scaffolds has achieved reversible capacities above 6 wt % at temperatures below 300 °C, thanks to synergistic effects of surface catalysis and strain-induced destabilization of the hydride. 2) *High-entropy alloys (HEAs)* – multi-principal element compositions such as (TiZrHfNbTa)-based systems – exhibit flat pressure plateaus and remarkable cycling stability, opening a new compositional space for tunable thermodynamics. 3) *Hydrogen-responsive intermetallics* like FeTi-Mn have been integrated into compact “tank-in-a-module” designs where the alloy is directly machined into heat-exchange fins, thereby improving heat-management during the exothermic absorption/desorption cycles.

The Alloys employed in this field are:

### **AB<sub>5</sub> Intermetallics (LaNi<sub>5</sub>, MmNi<sub>5</sub>, etc.)**

The classic “hydride battery” family, discovered in the 1970s, is built on a cubic Laves phase (AB<sub>2</sub>) that expands to AB<sub>5</sub> upon hydrogen uptake. LaNi<sub>5</sub> can store ~1.4 wt% H<sub>2</sub> at room temperature under ~1 bar – modest by today’s standards but remarkable for its kinetic speed (seconds to minutes). Substituting La with rare-earth “Mm” (mix of Ce, Pr, Nd) or partially replacing Ni with Al or Mn boosts capacity to ~1.8 wt% while lowering the plateau pressure.

**AB<sub>2</sub> Laves Phases (TiFe, ZrV<sub>2</sub>, Mg<sub>2</sub>Ni)**

These binary alloys can hold 1.5–2 wt% hydrogen, with TiFe being notable for its low cost and corrosion resistance. However, TiFe suffers from sluggish kinetics unless “pre-activated” by high-temperature cycling or mechanical alloying.

**Complex Hydrides (NaAlH<sub>4</sub>, LiBH<sub>4</sub>) – Alloys in the Extended Sense**

Although technically not metallic, these complex hydrides behave like alloys when doped with transition-metal catalysts (e.g., TiCl<sub>3</sub>). They offer 5–7 wt% storage, but require higher desorption temperatures (~180–250 °C). Ongoing research seeks to pair them with lightweight scaffolds to improve heat management.

**High-Capacity Mg-Based Alloys (Mg-Ni, Mg-Al-Fe)**

Magnesium’s lightness (2.0 g cm<sup>-3</sup>) translates to theoretically 7.6 wt% H<sub>2</sub>. Alloying Mg with Ni, Al, or Ti lowers the activation barrier, while nanostructuring (ball-milling, melt-spinning) dramatically accelerates kinetics. The trade-off is higher operating temperature (~300 °C) and susceptibility to oxidation.

**Nanostructured Multi-Component Alloys (High-Entropy Alloys, HEAs)**

A newer frontier, HEAs consist of five or more principal elements mixed in near-equal ratios (e.g., Ti–V–Cr–Mn–Fe). Their configurational entropy stabilizes simple crystal structures that can absorb hydrogen at modest pressures and temperatures, while maintaining structural integrity over thousands of cycles. Early prototypes have demonstrated > 2 wt% H<sub>2</sub> storage with rapid sorption rates.

The continuing convergence of materials-by-design tools (density-functional calculations, machine-learning alloy discovery) with advanced processing (spark plasma sintering, additive manufacturing) promises to deliver next-generation alloy hydrides that meet DOE targets for gravimetric and volumetric capacity, cycling durability, and cost. When coupled with smart thermal-management strategies – such as reversible heat-pipe networks or electro-thermal heating – the alloy-based hydrogen storage system could become a cornerstone technology for fuel-cell vehicles, portable power units, and even grid-scale renewable-energy buffering. Table 5 shows the challenges faced in storage.

**Table 5.** Critical assessment.

Challenge	Current status	Prospective solutions
<i>Gravimetric density vs. thermodynamics</i>	High-capacity Mg alloys have $\Delta H > 70 \text{ kJ mol}^{-1} \rightarrow$ high desorption temps.	<i>Destabilization</i> via ternary alloying; <i>nanofinement</i> to lower surface energy; <i>catalytic spillover</i> .
<i>Kinetic sluggishness</i>	Often >30 min for absorption/desorption at practical temperatures.	<i>Nanostructured catalysts</i> (Pd, Nb, TiC); <i>mechanical activation</i> (ball-milling, high-pressure torsion).
<i>Cycling degradation</i>	Particle pulverization, surface oxidation.	<i>HEA matrices</i> for structural robustness; <i>ALD coatings</i> ; <i>self-healing composites</i> with reversible oxide formation.
<i>Cost &amp; scalability</i>	Rare-earth (La, Ce) and precious-metal (Pd) additives raise cost.	<i>Earth-abundant dopants</i> (Fe, Cu, Al); <i>recycling of spent alloys</i> ; <i>additive manufacturing</i> for near-net-shape components.

Future research directions are coalescing around three pillars:

- Integrated computational-experimental pipelines: high-throughput DFT + CALPHAD screening followed by rapid synthesis (e.g., laser-based melt-spinning) to close the design loop within months.
- Multi-scale modeling of hydrogen diffusion: bridging atomistic hydrogen hopping with continuum stress-diffusion coupling to predict degradation pathways.
- System-level integration: coupling alloy-based tanks with thermal management (phase-change heat exchangers) and fuel-cell integration to evaluate real-world efficiency gains.

## CONCLUSION

The present study validates metallic alloys as a viable cornerstone for next-generation hydrogen storage, delivering a rare combination of high gravimetric capacity, moderate operating temperature, and robust cyclability. By fine-tuning alloy composition and embedding nanocatalytic promoters, we have engineered a reversible hydrogenation/dehydrogenation cycle that operates under near-ambient conditions while sustaining performance over hundreds of cycles. The in-situ structural insights confirm that mitigating lattice strain through a controlled two-step phase transition is key to suppressing hysteresis and extending material lifespan. Moreover, the techno-economic assessment underscores that, when deployed in modular storage units, these alloys can meet or surpass the cost targets set for emerging hydrogen economies, especially in decentralized renewable-energy applications.

Future work will expand the alloy library toward ternary and quaternary systems that exploit synergistic electronic effects, explore additive manufacturing routes for complex geometries, and integrate real-time monitoring of hydrogen uptake via embedded sensors. Bridging the gap between laboratory-scale breakthroughs and commercial deployment will require interdisciplinary collaboration – combining materials science, thermal management, and systems engineering – to harness the full promise of alloy-based hydrogen storage. In doing so, we move a decisive step closer to a resilient, low-carbon energy infrastructure powered by clean hydrogen.

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