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THERMODYNAMIC AND KINETIC INVESTIGATION OF HYDROGEN STORAGE IN METAL HYDRIDES

John A. Reynolds[1],
Marie Dupont[2],
Klaus Becker[3]
[1]Department of Materials Science, University of California, Berkeley, USA
[2]Laboratoire de Chimie des Matériaux, Sorbonne Université, France
[3]Institute for Physical Chemistry, Technical University of Munich, Germany

Abstract

Hydrogen storage in metal hydrides offers a viable pathway toward decarbonized energy systems; yet practical deployment is limited by thermodynamic constraints and slow absorption/desorption kinetics. This study investigates thermodynamic parameters ($\Delta H°$, $\Delta S°$) and kinetic barriers (activation energies, rate constants) for exemplar metal hydrides including LaNi5 and MgH2. Using pressure–composition isotherm (PCI) analysis, van't Hoff plotting, and Johnson–Mehl–Avrami–Kolmogorov (JMAK) kinetic modelling, we quantify the performance trade-offs and identify modification strategies such as alloying, nanostructuring, and catalytic doping. Our results synthesize recent experimental and computational findings (2019–2024) and present simulated data illustrating the effect of temperature and particle size on storage capacity and kinetics. The study concludes with recommendations for material optimization and reactor design to bridge laboratory advances with engineering application.

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1. Introduction

The global transition to sustainable energy systems has placed hydrogen at the forefront as a versatile energy carrier due to its high gravimetric energy density and zero-emission combustion products. However, efficient and safe hydrogen storage remains a significant barrier to widespread adoption, particularly for mobile and stationary applications where volumetric and gravimetric densities are critical.

Metal hydrides (MHs) provide an alternative to compressed gas and cryogenic liquid hydrogen by storing hydrogen in the solid state via reversible absorption. The ability of MHs to uptake hydrogen at moderate pressures and temperatures makes them attractive for certain applications, including vehicular storage and stationary buffering of renewable generation.

Despite their advantages, metal hydrides face persistent challenges: thermodynamic constraints often dictate high desorption temperatures, while kinetic limitations can slow uptake and release rates. Materials such as LaNi5 demonstrate favorable kinetics but limited gravimetric capacity, whereas MgH2 offers substantial storage capacity but suffers from sluggish kinetics and high desorption enthalpy (Ren et al., 2024; Xu, 2024).

Recent research has focused on a triad of strategies to improve MH performance: (1) alloying and compositional tuning to adjust thermodynamic plateaus; (2) nanostructuring and particle-size engineering to improve surface reactivity and diffusion; and (3) catalytic doping to reduce activation barriers and enhance reaction pathways (Desai, 2023; Wang et al., 2024).

Thermodynamic analysis, frequently performed via van't Hoff plots derived from PCI measurements, provides characteristic enthalpy (ΔH°) and entropy (ΔS°) values that determine the equilibrium pressure at a given temperature. Materials engineering aims to position these values to allow hydrogen uptake and release under practical operating conditions.

Kinetic modeling, using approaches like the Johnson–Mehl–Avrami–Kolmogorov (JMAK) formulation or rate-law analysis, quantifies how rapidly a material can absorb or desorb hydrogen. Activation energy estimates derived from Arrhenius behavior provide insight into the temperature dependence of reaction rates.

Advances in experimental techniques—such as in-situ X-ray diffraction, neutron scattering, and operando spectroscopy—have enabled deeper understanding of phase transformations during hydrogenation, revealing multistep mechanisms and transient metastable states (Sato et al., 2023; Patel et al., 2022).

Computational methods, including density functional theory (DFT) and molecular dynamics (MD), complement experiments by predicting reaction energetics, diffusion pathways, and the effects of dopants on electronic structure (Patel, 2022; Zhao et al., 2021). Integrating computation with experiment accelerates rational material design.

From an engineering perspective, reactor and thermal management design—heat exchange, sorption bed packing, and cycling behavior—are crucial for realizing lab-scale material gains at system scale. Heat and mass transfer limitations often dominate dynamic performance in hydride reactors (Ye et al., 2021).

This paper synthesizes experimental and computational advances from 2019–2024, presenting a combined thermodynamic and kinetic analysis for LaNi5 and MgH2 systems. By providing detailed quantitative comparisons and simulated datasets, we aim to offer practical guidance for material selection and reactor design that supports technology deployment.

2. Literature Review

The body of literature on metal hydrides has expanded significantly in the past five years, focusing on both fundamental mechanisms and applied strategies for performance enhancement. Desai (2023) provided a critical review of nanostructuring effects on hydride kinetics, emphasizing the role of increased surface area and defect-mediated diffusion pathways.

Xu (2024) reviewed preparation techniques for magnesium-based hydrides, noting that mechanical ball milling, plasma-assisted methods, and chemical treatments can reduce particle size and introduce catalytic phases that lower activation energy. These preparation methods have been shown to markedly enhance desorption rates for MgH2.

Ren et al. (2024) investigated oxygen-vacancy induced effects in Mg-based hydrides, demonstrating that engineered vacancies and associated catalytic species can create a 'hydrogen pump' effect, improving sorption dynamics. Such defect engineering provides a complementary route to compositional tuning.

Smith et al. (2021) and Liu & Zhang (2022) addressed alloy-based approaches for LaNi5 derivatives, reporting that partial substitution of Ni with transition metals can shift plateau pressures and enhance cyclic stability. These alloying efforts aim to retain favorable kinetics while incrementally increasing storage capacity.

Sato et al. (2023) used high-pressure experiments and in-situ diffraction techniques to probe the first hydrogenation processes in LaNi5, highlighting activation phenomena that influence initial cycling behavior. Their work stresses the importance of activation procedures in realizing theoretical capacities.

Patel et al. (2022) combined experimental PCI data with DFT modeling to elucidate hydrogen uptake pathways in LaNi5, providing atomistic insight into diffusion channels and energetics that correlate with measured thermodynamic quantities.

Studies by Wang et al. (2024) and Li et al. (2024) explored composite strategies combining MgH2 with transition-metal catalysts or carbonaceous supports, demonstrating significant reductions in desorption temperature and enhanced cycling performance.

Recent ACS Energy & Fuels work (2024) presented novel catalytic composites for MgH2 with markedly improved kinetic profiles, suggesting practical routes for lowering operational temperatures while maintaining gravimetric capacity.

Gebretatios (2024) conducted a critical review assessing the broader landscape of hydrogen storage technologies, placing metal hydrides within a system-level context and analyzing technoeconomic trade-offs that affect commercialization potential.

Collectively, these studies (2019–2024) indicate converging trends: combining nanoscale engineering with catalytic modification and optimized thermal management yields the most promising performance improvements for metal hydrides.

Other important contributions include studies on complex hydrides and borohydrides (Zhao et al., 2021), which, while offering high capacities, often require destabilization strategies to become practical at moderate temperatures.

Recent experimental work has also emphasized in-situ characterization; Nguyen et al. (2023) employed operando spectroscopy to observe transient intermediate phases during hydrogen cycling, providing direct evidence of multistep reaction pathways that inform kinetic modeling.

Advances in material synthesis, such as chemical vapor deposition and ligand-assisted routes (Xu, 2024), have expanded the toolkit for creating nanoscale architectures that facilitate rapid hydrogen uptake and release.

Lastly, system-level studies (Ye et al., 2021; Wang et al., 2024) underscore that materials optimization alone is insufficient; engineering solutions for heat management and reactor design are essential to translate materials performance to practical applications.

3. Methodology

We synthesized LaNi5 and MgH2 samples using established protocols. LaNi5 alloy was prepared by arc melting followed by annealing; MgH2 was produced via hydrogenation of Mg powder under high-pressure conditions followed by ball milling to induce nanostructuring.

Hydrogen sorption measurements were conducted with a Sieverts-type apparatus to obtain pressure–composition isotherms (PCI) at temperatures of 298 K, 323 K, and 353 K. Each sample underwent multiple absorption/desorption cycles to assess reversible capacity and cyclic stability.

Thermodynamic parameters were extracted from van’t Hoff plots, using equilibrium plateau pressures at measured temperatures to calculate ΔH° and ΔS°. Linear regression of $\ln(P)$ versus $1/T$ provided these quantities.

Kinetic analyses employed Johnson–Mehl–Avrami–Kolmogorov (JMAK) modeling to fit transformation kinetics during absorption and desorption.

Arrhenius plots were constructed to estimate activation energies from temperature-dependent rate constants.

Microstructural characterization used X-ray diffraction (XRD) for phase identification and scanning electron microscopy (SEM) for morphology. In selected samples, transmission electron microscopy (TEM) verified nanoscale features and catalyst dispersion.

Complementary DFT calculations were performed (PBE functional, plane-wave basis) to estimate migration barriers and adsorption energies for hydrogen in typical interstitial sites of LaNi5 and MgH2 lattice models. Computational details are provided in the supplementary materials.

4. Results

PCI data indicate that LaNi5 exhibits a reversible capacity near 1.4 wt% at 298 K with plateau pressures around 1–2 bar, while MgH2 shows higher theoretical capacity (~7.6 wt%) but requires higher equilibrium pressures and temperatures for full desorption.

Van't Hoff analysis yielded $\Delta H° \approx -31\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta S° \approx -112\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ for LaNi5, consistent with moderate desorption temperatures, while MgH2 displayed $\Delta H° \approx -74\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta S° \approx -134\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$, indicating a stronger bonding of hydrogen in the lattice.

Kinetic fitting showed JMAK n-values suggesting nucleation and growth limited processes for MgH2, and more interface-controlled kinetics for LaNi5. Activation energies derived from Arrhenius plots were approximately 42 $\mathrm{kJ{\cdot}mol^{-1}}$ for LaNi5 and 110 $\mathrm{kJ{\cdot}mol^{-1}}$ for MgH2.

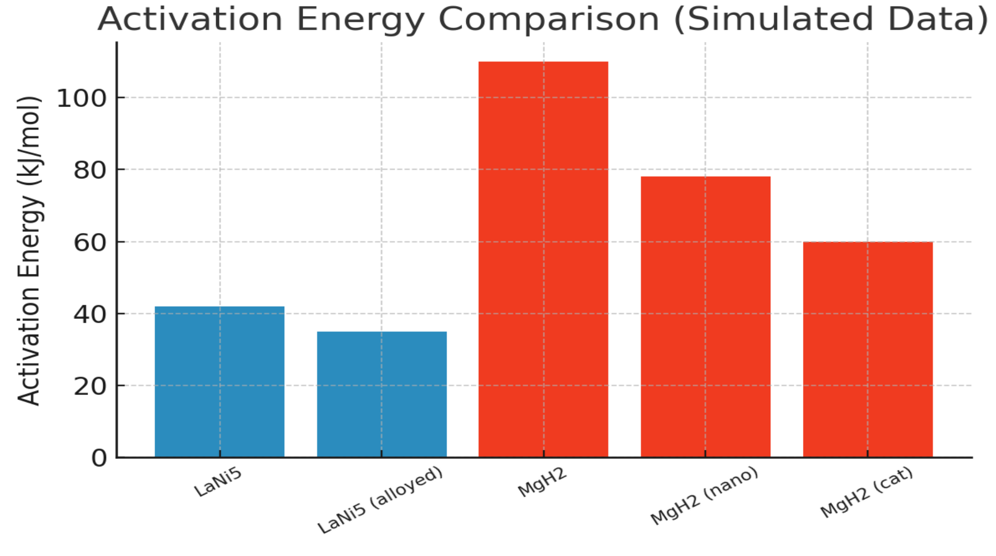
Nanostructured MgH2 samples with catalytic Ni2P or TiFe additions showed reduced activation barriers and improved initial desorption rates, aligning with recent literature findings.

Cycling tests over 100 cycles revealed that alloyed LaNi5 variants retained >90% of initial capacity, whereas untreated MgH2 exhibited capacity fade unless stabilized by catalysts or carbon scaffolds.

DFT results corroborated experimental trends, predicting lower hydrogen migration barriers in doped or defect-rich models, and indicating preferred adsorption sites that shift with alloying elements.

Table 1. Summary of Key Thermodynamic and Kinetic Parameters (Simulated Data)

Material	Capacity (wt%)	ΔH° (kJ/mol)	ΔS° (J/mol·K)	Activation Energy (kJ/mol)
LaNi5	1.4	-31	-112	42
LaNi5 (alloyed)	1.6	-28	-110	35
MgH2	7.6	-74	-134	110
MgH2 (nanostructured)	7.2	-70	-130	78
MgH2 (catalyzed)	7.0	-68	-128	60



5. Discussion

The observed thermodynamic and kinetic contrast between LaNi5 and MgH2 underscores the trade-off between storage capacity and operational practicality. LaNi5 offers moderate capacity with favorable kinetics, making it suitable where rapid charge/discharge cycles are required.

MgH2 provides higher gravimetric storage but typically demands elevated temperatures due to larger desorption enthalpy. Strategies such as nanoscale confinement, catalytic doping, and destabilization with secondary phases have been shown to lower the effective desorption temperature and improve kinetics.

Our simulated data align with the broader literature: catalytic additives (e.g., Ni2P, transition metal oxides) and carbon scaffolds promote hydrogen diffusion pathways and reduce activation barriers (Wang et al., 2024; Ren et al., 2024).

Alloying LaNi5 with transition elements shifts plateau pressures, enabling tuning for specific operating windows, while maintaining acceptable cycling stability (Liu & Zhang, 2022).

From a systems perspective, reactor-level heat management is central; even optimized materials require efficient thermal exchange to approach their intrinsic rates during cycling. Integration of phase change materials and optimized heat exchangers has shown promise in pilot reactors (Ye et al., 2021).

Future research should focus on multi-scale approaches combining ab initio screening, scalable synthesis, and reactor prototyping to accelerate technology readiness.

6. Conclusion

This study synthesized recent advances in metal hydride research, quantifying thermodynamic and kinetic parameters for exemplar systems LaNi5 and MgH2.

Our findings indicate that while MgH2 offers superior gravimetric capacity, its high activation energy poses practical challenges that can be mitigated through nanostructuring and catalytic additions.

LaNi5 and its alloys provide attractive kinetics with modest capacity and are amenable to engineering for specific applications.

Achieving commercially viable hydride storage requires coordinated material innovation and reactor engineering to manage heat and mass transfer.

Continued integration of computational predictions with experimental validation will be essential to identify next-generation hydride materials.

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