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Bio inspired design principles for next generation liquid organic hydrogen carriers: Bridging molecular biocatalysis and chemical hydrogen storage

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ABSTRACT

The Liquid Organic Hydrogen Carrier (LOHC) technology offers a highly promising way for large-scale hydrogen storage and logistics. LOHC systems combine high volumetric energy density with liquid-phase handling and compatibility with the existing fuel infrastructure. However, current LOHC systems typically require elevated temperatures and precious-metal catalysts for hydrogenation and dehydrogenation. By-products formed in hydrogenation/dehydrogenation can limit catalyst stability and repetitive use of the LOHC compounds. Furthermore, a significant amount of heat is typically required for hydrogen release, which limits overall efficiency if waste heat sources are unavailable.

In contrast, biological energy storage and hydrogen-conversion systems operate reversibly under mild conditions, relying on finely tuned redox cofactors, enzyme-controlled microenvironments and proton-coupled electron transfer pathways. By a comparative analysis of LOHC-based and biological hydrogen storage strategies, we highlight fundamental differences in how thermodynamic constraints are addressed at the process vs. at the molecular scale. Biological systems achieve near-reversible hydrogen conversion through precise tuning of redox windows, hierarchical energy storage and highly organized catalytic environments. LOHC technologies, in contrast, rely primarily on macroscopic control of temperature and pressure as will be exemplified for the N-ethylcarbazole/perhydro-N-ethylcarbazole LOHC system.

Our contribution identifies transferable design principles from biology, including microenvironment engineering, redox mediation and coupled reaction concepts. These principles could inspire next-generation LOHC-based storage systems and catalysts to achieve milder operating conditions, improved selectivity and enhanced energy efficiency, while preserving the scalability and robustness of chemical hydrogen storage.

1. Introduction

The global energy system is undergoing a profound transformation driven by the urgent need to mitigate climate change and achieve carbon neutrality within the coming decades. In this context, molecular hydrogen (H_2; hereafter referred to simply as hydrogen) is increasingly recognized as a key energy carrier due to its high gravimetric energy density, its ability to be produced from renewable resources, and its potential to decarbonize hard-to-electrify sectors, such as heavy-duty transport, aviation, and high-temperature industrial processes [1,2]. As a flexible energy vector, hydrogen can complement direct electrification and provide large-scale seasonal energy storage, thereby playing a central role in the transition to a sustainable energy economy [3].

Despite having the highest gravimetric energy density, the widespread use of hydrogen is hampered by challenges in its storage and distribution. In its molecular form, hydrogen exhibits a very low volumetric energy density under ambient conditions, necessitating compression to high pressures or liquefaction at cryogenic temperatures for storage and transport. Both approaches are energy-intensive and impose significant safety and infrastructure requirements [4]. Therefore, developing safe, scalable, and economically viable hydrogen

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storage solutions is essential for the establishment of a hydrogen-based energy system. So, material-based hydrogen storage technologies, where hydrogen is stored through physical adsorption or reversible chemical bonding. Although solid-state hydrogen storage materials can achieve high volumetric storage densities, their practical application is often constrained by slow kinetics, challenging thermal management, and the difficulty of handling solid materials [5]. Ammonia [6], methanol [7], dimethyl ether [8] or fuel like hydrocarbons produced via Fischer-Tropsch synthesis [9] are discussed as chemical hydrogen storage molecules. In these technologies, the hydrogen-lean molecule is a gas and must be provided from air before the synthesis of the hydrogen-rich molecule. In addition, recovering pure hydrogen after it is released is challenging, as hydrogen must be separated from the hydrogen-lean gas.

Liquid Organic Hydrogen Carriers (LOHCs) have emerged as a particularly promising approach to address these challenges [10–12]. In the LOHC concept, hydrogen is chemically bound to an organic compound through catalytic hydrogenation and released by dehydrogenation when needed. This approach combines high volumetric hydrogen densities at ambient conditions with the advantages of liquid handling, allowing the use of existing fuel infrastructure for storage and transport. An LOHC system should have a high hydrogen capacity, favorable thermodynamics, a wide liquid range, low toxicity and good commercial availability [13]. Since no LOHC molecule currently meets all these requirements, many different potential LOHC systems are being discussed. The most prominent LOHC systems are toluene/methylcyclohexane and benzyltoluene/perhydro benzyltoluene (Fig. 1b) [14–17]. These two hydrocarbon-based LOHC systems are currently being used in commercial demonstration projects for hydrogen storage and transport [18,19].

Since this review aims to discuss similarities and differences between chemical and biological hydrogen storage, we will focus on one specific LOHC system, namely the N-ethylcarbazole (H0-NEC)/perhydro-N-ethylcarbazole (H12-NEC) system (Fig. 1b). This selection has been made due to the structural similarity of this heteroaromatic/heteroalicyclic system to biologically relevant hydrogen storage systems. Although the gravimetric storage capacity of H0-NEC/H12-NEC is slightly lower than that of purely hydrocarbon-based systems, incorporation of nitrogen favorably modifies the thermodynamics of hydrogenation and dehydrogenation, thereby reducing the heat demand for hydrogen release and enabling operation at comparatively milder temperatures [26,27]. Hydrogen release from H12-NEC and hydrogen loading of H0-NEC are governed by intrinsic reaction enthalpies and equilibrium constraints, requiring elevated temperatures and pressure control at the process level. At the same time, the presence of C–N bonds can limit long-term robustness under repeated cycling. Improvements in catalyst selectivity or milder operating conditions may enhance stability, albeit typically at the expense of hydrogen release productivity [11,28–30]. Precious metal (Pd, Pt) nanoparticles supported on porous metal oxide or carbon supports are typically used for H0-NEC hydrogenation and H12-NEC dehydrogenation [31].

Biological energy storage, in contrast, uses a complementary design space, as organisms can natively interconvert H_2, CO_2 and organics at near-ambient temperature and pressure using finely tuned redox cofactors and protein catalysts. As biocatalysts or hybrid bioelectrocatalysts enable LOHC-type hydrogen storage reactions at ambient conditions, it is particularly interesting to take a ‘learning from nature’ to identify catalysts or storage systems enabling milder reaction conditions [32,33].

Biological H_2 conversion encompasses both hydrogen uptake and hydrogen release processes. Analogous to the hydrogenation step in LOHC technologies - hydrogenotrophic microorganisms use H_2 as a reductant to convert CO_2 into more reduced carbon compounds. Examples include acetogens, which produce acetate via the Wood–Ljungdahl pathway, methanogens, which produce methane, and aerobic hydrogen-oxidising (“Knallgas”) bacteria, which couple H_2 oxidation to O_2 reduction and CO_2 fixation. These organisms oxidise H_2 via hydrogenases and channel the released electrons into respiratory electron transport chains (truncated in case of anaerobes) or into reductive carbon assimilation pathways and biosynthesis. Owing to their ability to couple renewable H_2 directly to carbon fixation and chemical synthesis, these biological systems are increasingly exploited as catalytic platforms for gas-to-X upgrading and circular carbon processes [34–36]. H_2 release – analogous to the dehydrogenation step in LOHC technologies - ranges from dark-fermentative bacteria (e.g. *Clostridium* and *E. coli*) to photo fermentation- and microbial electrolysis cells. There have been ongoing advances in yields, substrate scope and process intensification [32]. Beyond immediate H_2 cycling, microbes deploy multi-time-scale energy storage. Long-term carbon/energy reservoirs, such as lipids (e.g. triacylglycerols), storage polysaccharides and polyhydroxyalkanoates (notably polyhydroxybutyrate), buffer fluctuating inputs and stabilize cellular metabolism. These storage pools - as well as fermentation-derived products - are now recognized as quantitatively relevant in both natural and engineered systems [37,38], including gas-fermentation platforms that couple H_2 oxidation with CO_2 fixation for chemical production. Recent industrial processes using acetogenic bacteria, such as the LanzaTech gas-fermentation technology for ethanol and isopropanol production from CO_2-rich off-gases, exemplify how microbial energy storage and redox flexibility can be harnessed at scale for carbon recycling and fuel synthesis [39]. Short- and medium-term cellular buffers rely on high-energy metabolites that couple catabolism to growth and anabolism. Examples include phosphoenolpyruvate (PEP) and 1,3-bisphosphoglycerate (1,3-BPG) in glycolysis and acetyl phosphate (AcP) in mixed-acid fermentation. These can generate adenosine triphosphate (ATP) through substrate-level phosphorylation and participate in global regulation [40]. At the core of biological energy transduction are energy-rich bonds, such as phosphoanhydrides (ATP) and thioesters (acetyl-CoA), whose prebiotic plausibility and centrality help to explain their universality and efficiency as cellular 'currencies' across life forms [41].

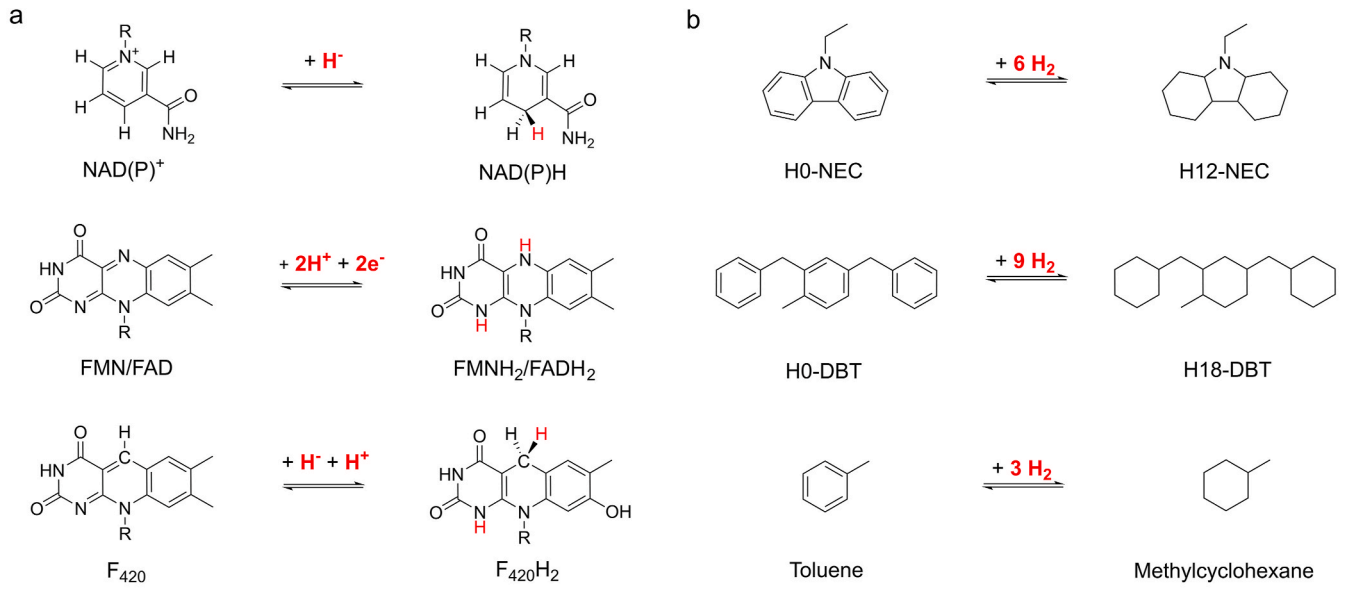
A defining feature of microbial energy metabolism is its cofactor and electron-carrier systems. Biological cofactors such as nicotinamide adenine dinucleotide (phosphate) ($NAD(P)^+$), flavin mononucleotide (FMN), flavin adenine dinucleotide (FAD) and Coenzyme F_{420} (F_{420}) are heteroaromatic redox scaffolds that enable selective proton-coupled electron and hydride transfer within enzyme-controlled microenvironments. Their reactivity is governed by heteroatom placement, conjugation patterns and local electrostatics, allowing reversible redox chemistry within a narrow physiological redox potential window [42,43].

In this review, we compare thermodynamics, catalysis concepts and molecular structures used in chemical and biological hydrogen storage systems. Our study aims to discuss possibilities to combine the advantages of both disciplines. For comparison, the relevant literature of both disciplines is summarized, and future research directions are derived from the comparison of both disciplines. Chemical hydrogen carriers have the advantage of significantly higher hydrogen storage capacities and higher robustness in technical processes. We argue that learning from nature, e.g., by considering cofactor-guided selectivity, the use of highly organized binding pockets to steer reactions, and the implementation of hierarchical energy storage cascades, can enable the development of catalysts and LOHC molecules with increased efficiency and minimized by-product formation while conserving the advantages of chemical hydrogen storage.

2. LOHC vs. biological storage molecules

2.1. Structural features of LOHC molecules

In principle, an LOHC system consists of at least one hydrogen-lean and one hydrogen-rich molecule. During hydrogen storage and release, the hydrogen-lean compound is hydrogenated, and the



c

Cofactor or Carrier	H_2 capacity (wt. %)	Free enthalpy#/ Hydrogenation enthalpy[2] (kJ mol^{-1} H_2)	E°' (pH 7)	References
$NAD(P)^+$/NAD(P)H	0.27-0.3	-18.1#	-0.32	[54]
$FMN/FMNH_2$& $FAD/FADH_2$	0.44 0.27	-37.4# -43.2#	-0.20 -0.22	[55]
$F_{420}/F_{420}H_2$	0.26	-14.3#	-0.34	[56]
$Ferredoxin/Ferredoxin_{red}$	-	-2.7 to +16.6#	-0.5 to -0.4	[57]
H0-NEC/H12-NEC	5.8	-50$	n. d.	[11]
H0-DBT/H18-DBT	6.2	-65.4$	-0.26	[58,59]
Toluene/ Methylcyclohexane	6.2	-68$	-0.25	[60]

Fig. 1. Molecular structures and properties of a selection of biological cofactors and LOHC molecules. a, Redox pairs of the nicotinamide cofactors NAD and NADP, the isoalloxazine cofactors FMN, FAD and F_{420}. **b**, Schematic representation of the LOHC systems *N*-ethylcarbazole (H0-NEC)/Perhydro-*N*-ethylcarbazole (H12-NEC), dibenzyltoluene (H0-DBT)/perhydro-dibenzyltoluene (H18-DBT) and Toluene/Methylcyclohexane. In red, the number of stored H_2 molecules is indicated. For clarity, only the protonated states of the **a** compounds after hydrogenation are shown. **c**, tabular representation of key parameters of biological cofactors and LOHC molecules. # Free enthalpy (ΔG° T = 298.15 K p = 1 bar H_2) of cofactor reduction. $ Enthalpy (ΔH° T = 298.15 K p = 1 bar) of LOHC hydrogenation [20–25].

hydrogen-rich compound is dehydrogenated. Both transformation steps require catalysts capable of activating H–H and C–H bonds. Aromatic compounds are frequently employed as hydrogen-lean molecules because their delocalized π-electron systems stabilize the unsaturated state and thereby facilitate reversible hydrogenation–dehydrogenation cycles [4].

For purely hydrocarbon-based LOHC systems, the reaction enthalpy of dehydrogenation typically lies in the range of 65–70 kJ mol^{-1} H_2 [44]. While this allows safe hydrogen storage, it necessitates substantial heat input for hydrogen release. Incorporation of heteroatoms offers a strategy to tune these thermodynamic parameters. In the heteroaromatic N-ethylcarbazole (H0-NEC)/perhydro-N-ethylcarbazole (H12-NEC) system — one of the most intensively studied nitrogen-containing LOHC pairs — the dehydrogenation enthalpy is reduced to approximately +50 kJ mol^{-1} H_2 [11,26,45,46]. This decrease in reaction enthalpy lowers the heat demand for hydrogen release and enables operation at significantly reduced temperatures compared to hydrocarbon systems. At the same time, the gravimetric hydrogen storage capacity of the H0-NEC/H12-NEC pair amounts to 5.8 wt%, slightly lower than that of purely hydrocarbon-based carriers [11]. Dehydrogenation of H12-NEC is typically conducted at 150–250 °C and hydrogen partial pressures of 1–5 bar [27], whereas hydrogenation of H0-NEC generally requires 100–200 °C and 30–80 bar H_2 [29,30]. Although nitrogen incorporation improves thermodynamic favorability, the presence of C–N bonds can reduce thermal robustness and cycle stability due to cleavage reactions under prolonged operation [28]. Enhancing catalyst selectivity or operating under milder conditions may increase cycle numbers, but usually at the expense of hydrogen release productivity for kinetic and thermodynamic reasons.

2.2. Structural features of biological cofactors ($NAD(P)^+$/H, FMN/FAD and F_{420})

Biological cofactors such as NAD(P), FMN, FAD and F_{420} have complex polycyclic heteroaromatic structures derived from vitamin precursors such as nicotinamide, riboflavin and deazaflavin (Fig. 1a). The placement of functional heteroatoms (notably nitrogen) including functional groups enables highly selective proton-coupled electron transfer (PCET) and hydride transfer under mild aqueous conditions when paired with their cognate biocatalysts. These scaffolds combine redox centres and proton relay networks, enabling reversible electron exchange with minimal overpotential under physiological redox potential range.

In NAD(P), site-specific hydride transfer to the nicotinamide C4 is controlled by orbital alignment and local protonation networks of biocatalysts. This enables high regioselectivity and minimizes side products. Kinetic and mechanistic studies (including stepwise proton transfer/hydride transfer sequences) underscore how protein environments bias the reaction path [47–49], which is directly relevant to selective LOHC (de)hydrogenation. Recent studies with non-canonical nicotinamide cofactors demonstrate how modifications to the nicotinamide core or the use of simplified models can shift redox potentials and hydride/PCET activity into new ranges [50,51]. Flavins (FMN, FAD), embedded as prosthetic groups in many oxidoreductases, utilize the isoalloxazine tricycle to mediate one- and two-electron transfers via proton-coupled electron transfer. Reactivity is modulated by functional groups surrounding N5 and the C4=O4 carbonyl, which influence the balance between radical and hydride pathways. These principles have inspired synthetic flavins with expanded π-systems to tune redox potentials and stability [52–54]. The deazaflavin F_{420}, which lacks N5, shifts towards low-potential, two-electron hydride chemistry while suppressing single-electron transfer. Its growing biocatalytic interest and scalable precursor production highlight a biocompatible, selective hydride currency that together with NAD(P)H thermochemical LOHC cycles currently struggle to emulate without the use of high temperatures or precious metals [55]. Ferredoxins, small iron–sulfur proteins operating at very low redox potentials, illustrate how biological systems access highly reducing chemistry through modular electron carriers [56]. However, their low hydrogen-storage capacity and biochemical complexity preclude their use as bulk hydrogen carriers.

2.3. Structural comparison: What to learn from biological hydrogen storage systems?

A critical paradox in LOHC chemistry is the trade-off between stability and reactivity: carriers or catalysts must be sufficiently reactive to enable efficient hydrogenation or dehydrogenation. However, high reactivity can expose them to decomposition, side reactions or loss of selectivity, particularly during repetitive hydrogenation/dehydrogenation cycles or in the presence of impurities such as oxygen, water or radical species. Nature resolves this trade-off through enzymatic microenvironments that protect reactive cofactors. Protein active sites encapsulate heteroaromatic cores (e.g. NAD(P), FMN, FAD and F_{420}), exclude harmful agents within the binding pocket, stabilize protonation states via hydrogen bonding, and reduce the formation of reactive radicals or undesirable by-products. A study of non-canonical redox cofactors highlights this principle at a synthetic level. Engineering a glucose dehydrogenase to utilize nicotinamide mononucleotide instead of the natural cofactor $NAD(P)^+$ enabled highly efficient recycling of the cofactor with turnover numbers exceeding 39,000 in vitro and in whole-cell systems, without compromising the performance of the synthetic cofactor [57]. Recent NAD(P)H-mimetic and electrocatalytic regeneration studies show that regioselective 1,4-reduction and mediator stability remain persistent bottlenecks. Biology's solutions - preorganised heteroaromatics, proton relays and protein binding pockets for NAD(P)H - suggest concrete strategies: embed H-bond/proton channels near the reactive centre, use rigid, heteroatom-rich π-cores to enforce hydride delivery geometry and operate within narrow redox potential windows to suppress off-pathway reactions [48,58]. In parallel, biohybrid schemes that couple ferredoxin-like carriers to synthetic catalysts demonstrate that tuneable redox carriers can deliver high H_2 conversion rates under mild conditions [59]— an attractive contrast to many LOHC systems that still require elevated temperatures, especially for dehydrogenation. However, biological hydrogen carriers often have limited hydrogen storage capacity, which is a decisive parameter in the economic evaluation and comparison of different carrier molecules. It is, therefore, crucial to transfer the advantageous structural features of biological hydrogen carriers to less complex structures to enable higher hydrogen storage capacities. Overall, the heteroaromatic, cofactor-centred design logic of biochemical systems provides a transferable blueprint for next-generation LOHC systems aiming for enabling milder reaction conditions and better reversibility under practical conditions through PCET-enabled selectivity at low overpotential (Fig. 2). By comparing these biological redox systems, we can derive structural and thermodynamic design rules for future biology-inspired LOHC systems: (i) How to position heteroatoms to tune the redox potential and pathway (hydride versus radical); (ii) how to couple electron carriers with catalytic systems to achieve reversible and efficient hydrogen storage under mild conditions.

3. Thermodynamics and redox potentials

3.1. Thermodynamics in LOHC systems

Knowledge of the thermodynamic equilibrium is essential for defining suitable reaction conditions for hydrogen loading or release. At constant temperature, the direction of reaction - hydrogenation or dehydrogenation - can be shifted simply by adjusting the reaction pressure [60]. The Gibbs free energy, which is minimal close to the chemical equilibrium, is determined by the standard reaction enthalpy and entropy. For the H12-NEC/H0-NEC system, both parameters have been experimentally quantified, enabling accurate estimation of the

Gibbs free energy and thus the equilibrium composition [61–63]. Building on these thermodynamic data, Heublein et al. calculated the equilibrium composition of the H0-NEC/H12-NEC mixture and experimentally validated a quasi-equilibrium state, with sufficiently good agreement between estimation and measurements [64].

As expected for reversible hydrogenation systems, low temperatures favor thermodynamically the exothermic hydrogenation of H0-NEC to H12-NEC, while high temperatures shift the equilibrium toward endothermic dehydrogenation. Because hydrogenation reduces the total number of molecules, elevated pressures are thermodynamically advantageous for hydrogenation. Conversely, dehydrogenation generates additional molecules, making low pressures thermodynamically favorable for hydrogen release. These general trends apply to all LOHC systems. Compared to pure hydrocarbon LOHC systems such as toluene/methylcyclohexane or benzyltoluene/perhydro-benzyltoluene, the NEC-based system exhibits a lower equilibrium temperature for dehydrogenation and a higher equilibrium pressure for hydrogenation [17].

However, process conditions cannot be selected based solely on thermodynamic considerations. Catalyst activity, heat-transfer characteristics, by-product formation and LOHC stability, as well as economic constraints, must be also taken into account for defining suitable operating windows for practical hydrogen loading and hydrogen release processes.

3.2. Thermodynamics in biological hydrogen and energy storage

Biological hydrogen converting cofactor dependent biocatalysts operate under remarkable thermodynamic constraints, by precisely tuned, reversible redox couples. Cellular energy transduction relies on redox cofactors such as NADH/NAD^+, NADPH/$NADP^+$, $FMNH_2$/FMN, and ferredoxin, whose midpoint potentials span a carefully orchestrated range (Fig. 1c), ensuring directionality while minimising energy losses [65,66]. These potentials are reversible under physiological conditions, enabling both energy capture (e.g. H_2 oxidation feeding electrons into respiratory chains) and energy storage (e.g. CO_2 reduction to organic products). Notably, the tuning of E_m values in the case of ferredoxins often arise from protein microenvironments that shift standard cofactor potentials via local dielectric effects and hydrogen bonding. Recent studies using protein film electrochemistry and ultrafast spectroscopy have revealed how small structural changes can modulate redox potentials by tens of millivolts, enabling in situ adaptation to metabolic or environmental demands [67]. As summarized in Fig. 1c, LOHC systems and biological cofactors differ markedly in their redox properties and reaction reversibility. Biological hydrogen carriers operate via enzyme-catalyzed reactions that are often fully reversible. For example, [NiFe]-hydrogenase enzymes can catalyse both H_2 oxidation and proton reduction under physiological conditions. This means the same enzyme can alternately produce or consume H_2 (i.e. $H_2 \rightleftharpoons 2H^+ + 2e^-$) with minimal overpotential, a feature confirmed in cyanobacterial bidirectional hydrogenases (which function bidirectionally in H_2 metabolism) and in NAD^+-reducing hydrogenases from the Knallgasbacterium *Cupriavidus necator* [68,69]. The bidirectional hydrogenase of *Synechocystis* sp. (PCC6803) is an electron sinks for low potential electrons from photosystem I and acts as a redox balancing device under fermentative conditions. These biological systems leverage well-defined cofactor redox potentials to tune reaction thermodynamics: for instance, the NAD^+/NADH couple is slightly less reducing than H_2, so H_2 generation from NADH is mildly endergonic (Fig. 1c). In living cells this hurdle is overcome by coupling reactions or using low-potential electron donors – ferredoxin can drive H_2 formation exergonically (Fig. 1c) – often via electron bifurcation that combines high- and low-potential electrons in one enzymatic step. One exergonic and one endergonic electron transfer are driven simultaneously — hereby, coupling H_2 oxidation to both low-potential ferredoxin and high-potential NAD^+ reduction — thereby maximising energy recovery [65].

These principles highlight a key lesson for LOHC systems: Reaction thermodynamics can be locally manipulated by the optimal design of the microenvironment around the catalytically active site (Fig. 2). Such microenvironments create reactant concentrations that differ from the bulk, thereby enabling hydrogen release even under thermodynamically unfavorable bulk conditions. Mimicking biological strategies, such as precisely adjusted redox windows, low overpotentials and kinetic acceleration under mild conditions, could help to further tune reactivity of LOHC systems also at much milder process conditions.

3.3. Combining thermodynamic concepts in chemical and biological hydrogen storage

The comparison of LOHC-based hydrogen storage systems with biological hydrogen-converting pathways reveals a striking conceptual overlap, despite the fundamentally different nature of the underlying chemistries. In both cases, reversible hydrogenation and dehydrogenation reactions are governed by well-defined thermodynamic equilibria, which ultimately dictate the attainable operating windows, efficiencies and degrees of reversibility. However, the manner, in which these thermodynamic constraints are addressed differs profoundly between technical LOHC systems and biological energy storage.

In LOHC systems, thermodynamic control is predominantly exerted at the macroscopic process level by controlling temperature, pressure and the concentration of the reactants. However, thermodynamics can never be considered in isolation as the boundary conditions of the technical operation require compromises between thermodynamic driving forces, kinetics, heat-transfer and material stability aspects. The resulting operating conditions are therefore often far from thermodynamic ideality.

Biological systems, in contrast, operate close to thermodynamic reversibility by exploiting finely tuned redox potentials at the molecular scale. Enzyme-catalyzed hydrogen conversion is embedded in networks of redox cofactors whose reactivity and redox potentials are adjusted by protein matrix, PCET pathways, electronic coupling and dynamic mechanisms such as electron bifurcation. Rather than overcoming unfavorable equilibria through large external driving forces, biological systems minimize energy losses by matching redox levels with remarkable precision and by kinetically accelerating reactions at minimal overpotentials (Fig. 2). This allows bidirectional operation and enables rapid adaptation to changing metabolic demands.

The juxtaposition of these two approaches highlights a central insight: thermodynamic optimization cannot be decoupled from catalyst and system design. While LOHC technologies currently rely on macroscopic control variables, biological systems demonstrate how thermodynamic constraints can be managed at the level of the catalyst microenvironment. This review suggests that future advances in LOHC technology may benefit from shifting part of the optimization problem from the process scale toward the molecular and mesoscopic scales.

4. Catalytic strategies for LOHC systems: chemical, biological, and biology-inspired future approaches

4.1. Heterogeneous catalysts for the LOHC system N-ethylcarbazole/perhydro N-ethylcarbazole

Heterogeneous catalysts are essential for enabling the reversible hydrogenation and dehydrogenation of LOHC systems [70]. Optimal catalytic performance requires a well-balanced adsorption strength of reactants and products on the catalyst surface [71]. Insufficient adsorption leads to low surface coverage and hinders activation of fresh reactants. Conversely, excessively strong binding impedes product desorption, blocks active sites, and facilitates undesired consecutive reactions that reduce selectivity and promote catalyst deactivation. In LOHC catalysis, supported precious-metal catalysts are widely used. The type and dispersion of the active metal, as well as the nature and texture of the support, decisively influence adsorption behavior and thus

catalytic activity and selectivity. Because adsorption characteristics depend strongly on the LOHC structure, catalysts must be tailored specifically for each LOHC system. In addition, the support must be selected in a way that ensures fast diffusion of the LOHC compounds to and from the catalytic site at the supported metal nanoparticles. Side reaction induced by support reactivity with any of the LOHC compounds present in the storage/release cycle should be strictly avoided. In the following, catalysts for the hydrogenation of H0-NEC and the dehydrogenation of H12-NEC are discussed.

Catalysts based on Ru, Rh, and Pd have been investigated for the hydrogenation of H0-NEC, with Ru consistently identified as the most active metal under typical process conditions, followed by Rh and Pd [72–74]. As low coordinated reaction sites are the most active, Ru particle size plays a central role in catalytic performance. Tailoring the size and dispersion of Ru clusters enables significant optimization of hydrogenation activity [75,76]. Incorporation of secondary transition metals such as Co, Fe, or Ni into Ru catalysts can enhance activity by altering the electronic structure of Ru and facilitating adsorption of intermediate hydrogenation species such as H8-NEC, the rate-determining intermediate [72,77]. Pure Ni-based catalysts offer a cost-effective alternative due to the much lower price of Ni. However, their activity is substantially lower than that of Ru-based systems [78,79]. The hydrogenation of H0-NEC proceeds via the stable intermediate stages H4-NEC and H8-NEC to H12-NEC. Fundamental insights into the hydrogenation pathway on a Ni(111) surface based on density functional theory (DFT) calculations were given by Li et al. [80]. First, the six-membered-rings react with hydrogen as the energy barrier (0.42 to 0.82 eV) is lower compared to the hydrogenation of the five-membered-ring (1.26–1.57 eV). This means that the hydrogenation of H8-NEC is the rate-determining step in hydrogenation of H0-NEC.

The support strongly affects hydrogenation activity. Among the tested porous support materials, alumina exhibits the best performance for H0-NEC hydrogenation due to its favorable acidity, porosity, and metal–support interaction [81].

Hydrogenation of H0-NEC yields only partially hydrogenated intermediates and the fully hydrogenated product H12-NEC. Side reactions, such as cleavage or oligomerization, are commonly not observed. Therefore, catalyst optimization focuses primarily on increasing activity and stability rather than selectivity. Catalyst deactivation during repeated hydrogenation cycles has been reported and can largely be attributed to sintering of Ru particles at elevated temperatures [82,83].

For the dehydrogenation of H12-NEC, supported precious-metal catalysts based on Pd and Pt are predominantly used, with Pd typically showing the highest activity, followed by Pt [84,85]. Other precious metals such as Ru, Rh, or Au show considerably lower activity and are therefore of limited relevance for H12-NEC dehydrogenation. The same stable intermediates as in hydrogenation can be detected in the dehydrogenation of H12-NEC on a Pd(111) surface [86]. First, hydrogen is released from the five-membered-ring (0.25–0.53 eV) and afterwards from the six-membered-rings (0.16-0.84 eV) [87]. Furthermore, it was estimated based on DFT calculations that Ni is catalytically inferior to Pd due to a narrower d-band distribution and a higher d-band center.

Catalytic activity in dehydrogenation strongly depends on the size of the metal nanoparticles [88]. Consequently, bimetallic catalysts have been developed to control particle size or to create synergistic electronic and geometric effects that enhance activity [89,90]. Similar to hydrogenation, the support material plays a crucial role. For H12-NEC dehydrogenation, carbon-based supports are the most active, followed by alumina and titania [91,92]. Because mass transfer limitations can significantly affect activity, egg-shell catalysts—where the active metal is only located in the outer volume of a given catalyst pellet to shorten the critical diffusion path length - are particularly effective in improving precious-metal utilization [93].

Compared to pure hydrocarbon LOHC systems, catalyst deactivation in H12-NEC dehydrogenation is typically less pronounced due to the milder process conditions. Stable operation over more than 200 h has been successfully demonstrated [94]. In contrast, the much harsher dehydrogenation conditions that have to be applied in the case of pure hydrocarbon LOHC systems for thermodynamic reasons have been shown to cause severe catalyst deactivation, in particular if complete hydrogen discharge is targeted [95,96]. However, it is fair to state, that also H12-NEC undergoes notable decomposition under dehydrogenation conditions, leading to cleavage of the carrier molecule and formation of non-rehydrogenable fragments [28,97]. Decomposition represents a critical challenge because it irreversibly consumes the LOHC molecule. Pure hydrocarbon LOHCs are generally more stable in this respect [98]. Thus, catalyst development for NEC dehydrogenation focuses strongly on suppressing molecular cleavage. A promising way towards this goal is hydrogen release at lower temperature, where thermally induced decomposition pathways are less pronounced [99].

A central goal in LOHC technology is the development of catalysts that remain active under milder reaction conditions. Lower temperatures reduce by-product formation and enhance the cycle stability of the LOHC material. In LOHC dehydrogenation, low-temperature operation limits the pressure at which hydrogen can be released but increases opportunities to utilize industrial waste heat or heat from fuel cells or engines to drive the endothermic reaction. In hydrogenation, milder conditions mitigate sintering and thereby improve catalyst stability. However, lowering the hydrogenation temperature reduces the potential to use the released hydrogenation heat in other processes.

4.2. *Biological catalysis: Enzyme-based selectivity and Efficiency*

Biological H_2 conversion relies on hydrogenases, which are a diverse class of metalloenzymes that catalyse the reversible interconversion of protons, electrons and molecular hydrogen with remarkable selectivity and efficiency under mild, aqueous conditions [100]. Three major types are distinguished based on active site composition: Fe-only, [NiFe]- and [FeFe]- hydrogenases (Fig. 2). The last two classes employ heterolytic H_2 splitting coupled to PCET and transfer electrons across chains of FeS-clusters [100]. These cofactors are composed of Fe, Ni and S-atoms that are among the most abundant in the Earth's crust. This stands in sharp contrast to many LOHC catalysts, which rely on precious metals such as Pt, Pd or Ru, metals that are scarce, expensive, and geopolitically constrained.

Hydrogenases contain well-defined metallocofactor sites (around one kDa in total of structured metal–ligand environment within proteins of 40–100 kDa in the case of the basic hydrogenase module). Although these active sites are much larger than the atomic or few-atom catalytic centres used in chemical H_2 catalysts, they nevertheless achieve high turnover frequencies, often above 1000 s^{-1} at room temperature and with minimal overpotential [100]. Hydrogenases achieve this performance under mild, aqueous conditions through precisely organised metal coordination, proton-transfer pathways, and electron-relay networks. This efficiency contrasts sharply with the high temperatures often required in purely thermochemical hydrogenation–dehydrogenation cycles used in LOHC systems [4]. However, the operation in an aqueous environment is often disadvantageous in the context of hydrogen logistics as the water would lower the hydrogen storage capacity or would require additional separation of the organic and aqueous phase.

The structural motifs enable near-reversible catalysis at overpotentials close to zero, providing a performance comparable to that of platinum-group catalysts in H_2 activation, but under biologically compatible conditions. Hydrogenases operate under remarkable mild constraints, achieving efficient energy interconversion at ambient temperatures and pressures. They accelerate redox and energy-transfer reactions by many orders of magnitude compared to uncatalyzed processes, thereby lowering activation barriers while preserving

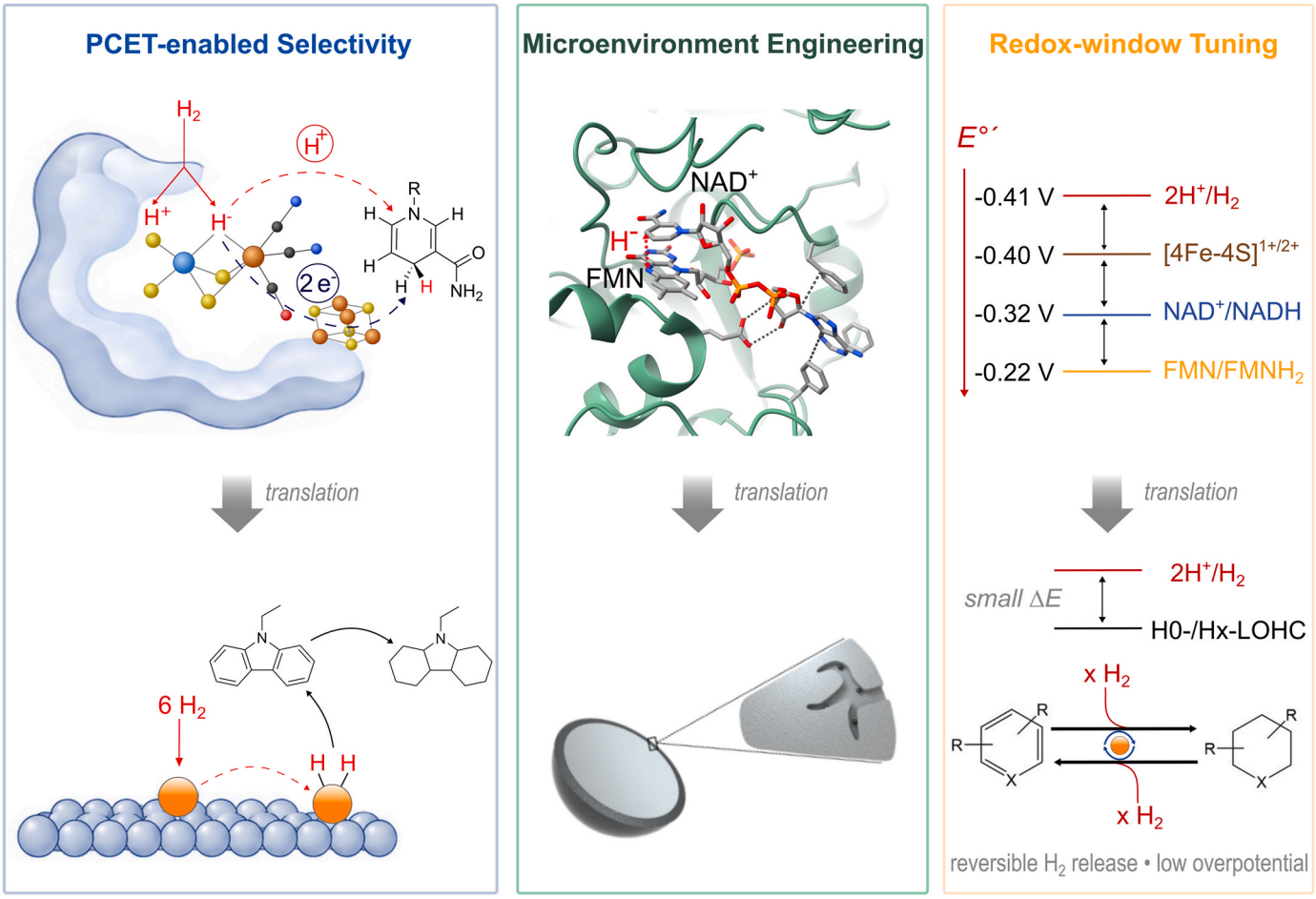


Fig. 2. Bio-inspired design blueprint for LOHC catalysis. Biological hydrogen-conversion systems combine proton-coupled electron transfer (PCET), precisely structured catalytic microenvironments, and finely tuned redox windows to enable selective and reversible reactions under mild conditions. Translating these principles to LOHC catalysis suggests the design of selective proton and electron transfer pathways, engineered catalyst microenvironments, and redox-matched carrier–catalyst pairs. Their combined implementation may facilitate milder operating conditions, suppress side reactions, and improve cycle stability.

thermodynamic driving forces.

A hallmark of hydrogenases is their functional integration into biochemical redox networks. Many hydrogenases directly couple to electron carriers such as NAD(H), ferredoxin (Fdx) or F_{420}, ensuring efficient energy conversion for metabolism and redox homeostasis [101,65]. Chimeric designs, such as hydrogenase–formate dehydrogenase fusion enzymes, exploit these principles to produce formate through hydrogenation of CO_2 at ambient conditions significantly lowering the necessary hydrogen pressure compared with thermochemical processes [102]. One instructive example is the oxygen-tolerant soluble [NiFe] hydrogenase from *Cupriavidus necator*, which combines high catalytic activity with remarkable stability in the presence of O_2 and CO [68,103]. Its bimetallic [NiFe] center, coordinated by CO and CN ligands, enables efficient H_2 oxidation while maintaining reversible redox control. Electron transfer to NAD^+ is mediated through an integrated Fe–S and flavin relay, allowing rapid hydride delivery with minimal energy dissipation [66,104]. Protective catalytic mechanisms further mitigate oxidative damage [103,105,106]. Recent studies on reverse electron transfer demonstrate the flexibility of these enzymes' thermodynamics, showing that they can catalyse uphill reactions such as H_2 evolution from NADH under defined bio-chemical-conditions [68]. Together, these features illustrate how catalytic efficiency and robustness can be reconciled through precise structural and electronic organization — a balance that remains challenging in thermochemical LOHC catalysis.

4.3. Toward bio-inspired and hybrid catalysis

Bio-inspired catalyst design aims to transfer the exceptional selectivity, efficiency and mild operating conditions of enzyme systems to thermochemical catalysts. In the context of LOHC technologies, the activity of hydrogenases at low temperature needs to be applied to supported precious metal nanoparticles. Recent reviews of LOHC catalysis highlight that, although noble metal catalysts (e.g. Pt, Ru and Pd) can achieve high levels of activity, they are expensive and often require a high dehydrogenation temperature or elevated hydrogen pressure in hydrogenation [107]. Remarkable progress has been made in catalysis engineering to improve precious metal utilization, stability and selectivity [108,109]. Nevertheless, the catalytic barriers remain high, as demonstrated by DFT studies on H12-NEC dehydrogenation, in which desorption steps exhibit activation barriers of up to ~255 kJ mol^{-1} [110].

Hydrogenases provide several design lessons for LOHC catalysis. Firstly, the active-site microenvironments of enzymes use protein matrices to control solvent access, stabilize reactive intermediates and shield catalytic centres from oxidative inactivation — a principle that can be translated to synthetic catalysts via ligand shells, porous supports or hybrid organic–inorganic frameworks [100]. The formation of coke precursors is a known problem in the dehydrogenation of perhydro-benzyltoluene [111] and other aromatic and heteroaromatic LOHC compounds. Coke precursors oligomerize to coke, which leads to catalyst deactivation. Prevention of re-adsorption and thus

oligomerization of the coke precursors might be one possible effect of a better control of the catalyst's microenvironment. Secondly, hydrogenases use [FeFe] or [NiFe] active sites and iron–sulfur clusters to mediate stepwise, low-overpotential electron and proton delivery; introducing redox mediators or bifunctional supports in LOHC catalysts could similarly lower reaction temperature and thus improve selectivity [112]. Thirdly, electron bifurcation in enzymes enables the coupling of one exergonic and one endergonic process to maximise energy recovery [102]. Analogous hybrid LOHC catalysts might couple dehydrogenation with internal redox cycles to lower activation energy and improve kinetics. Finally, second-sphere interactions, such as hydrogen bonding, local polarity tuning and acid–base residues, enhance stability of intermediates and modulate activation energy in enzymes [106]. This suggests that controlled catalyst microenvironments could improve performance and suppress side reactions (Fig. 2).

4.4. Industrial realism and scalability constraints

Biological conversion processes can be implemented at industrial scale. The large-scale production of biomethane and bioethanol demonstrates the technical scalability of biological routes for energy-carrier production. Although these processes are not directly comparable to reversible LOHC cycles, they demonstrate the technical scalability of biological routes for energy-carrier production.

A more relevant benchmark is the industrial application of Fe- or Co-dependent nitrile hydratases for the selective conversion of acrylonitrile to acrylamide. Reported production capacities have increased from approximately 30,000 t a^{-1} to more than 600,000 t a^{-1}, illustrating that metalloenzymes can support commodity-scale chemical manufacturing [113]. Biological H_2 conversion likewise relies predominantly on comparatively abundant metals such as Fe and Ni, whereas established LOHC catalysts frequently depend on scarce platinum-group metals, including Pt, Ru and Pd. Nevertheless, enzyme production, stabilization and operational lifetime remain important constraints. Bio-inspired LOHC concepts should therefore not aim at the direct replacement of heterogeneous catalysts by natural enzymes, but rather at the transfer of selected principles, including microenvironment control, PCET-enabled selectivity and redox-window tuning, into scalable synthetic catalyst systems benchmarked against Pt- and Pd-based technologies.

5. Summary and perspectives

5.1. Key insights and comparative highlights

This review has contrasted hydrogen storage using LOHCs with biological energy storage systems with a focus on molecular structure, thermodynamics, and catalysis. LOHC systems such as toluene/methylcyclohexane or N-ethylcarbazole/perhydro-N-ethylcarbazole offer high volumetric hydrogen densities in liquid form and are compatible with the existing infrastructure for liquid fuels. However, depending on the charging and release conditions, the formation of by-products limits the achievable amount of storage cycles. Additionally, LOHC technology typically requires elevated temperatures, precious-metal catalysts and substantial energy input for dehydrogenation, which significantly influences the costs for hydrogen or energy provision from these storage systems. The high heat demand for dehydrogenation and the precious metal-based catalyst leads to the fact that operating expenditures (OPEX) are typically higher than capital expenditures (CAPEX) of a dehydrogenation plant [114,115]. The dehydrogenation temperature might be significantly reduced by finely tuning redox potentials at the molecular scale as suggested by biological systems. The lowering of dehydrogenation temperature enables heat integration with cheaper waste heat sources, which significantly reduces OPEX due to the lower costs for heat provision. Furthermore, analogous hybrid LOHC catalysts that translate biocatalystic design principles into technical catalyst systems could reduce the reliance on rare precious metals, potentially lowering catalyst costs and further decreasing OPEX.

Biological systems, by contrast, operate with heteroaromatic cofactors (NAD(P), FMN, FAD, F_{420}) and protein-embedded metal centres (e.g. [NiFe] and [FeFe] hydrogenases) whose redox potentials are finely tuned for reversible hydrogen and electron transfer under mild, aqueous conditions. These cofactors and enzymes achieve high selectivity and low overpotential through pre-organised binding pockets, proton-relay networks and carefully adjusted redox windows. Although biological cofactors are far too expensive and have too low hydrogen capacity to serve directly as compounds in technical LOHC systems, they exemplify design principles - PCET-enabled reactivity, controlled microenvironments, and earth-abundant metal usage - that are highly relevant for improving LOHC technologies in future research.

A central insight is that the design of the catalyst microenvironment for adjusting local concentrations and thus thermodynamic driving forces has to go hand-in-hand with the structural optimization of the respective catalytic site for enhanced kinetics. Biological hydrogen carriers and hydrogenases show how precise tuning of redox potentials, coupled electron–proton transfer and local environment control can minimize energy losses and enable reversible operation. Translating these concepts to LOHC chemistry suggests that future research should target to enable milder operating conditions and lower overpotentials to enable improved selectivity and longer service times.

An interesting alternative to thermocatalysis is electrocatalysis, which can also profit by learning from nature. Hydrogenases also interface effectively with electrochemical platforms. Membrane-bound [NiFe] hydrogenases can be directly wired to electrodes - via conductive surfaces or redox polymers - enabling fast and reversible H_2 oxidation or evolution with minimal overpotential [116]. Work with redox-polymer-wired hydrogenases has further shown sustained direct electron transfer on electrodes under quasi-physiological conditions [117]. These studies demonstrate how protein microenvironments and FeS relays can be electrically addressed to achieve highly efficient bioelectrocatalysis. Hybrid and bio-inspired strategies, including redox mediators, structured catalyst environments and integrated electro-biocatalytic schemes, have the potential to enable the described future research goals.

5.2. Future research directions

The overall goal of bioinspired research on LOHC technology is to enable milder reaction conditions, which can improve selectivity and simplify heat integration for hydrogen release thus improving system efficiency. However, it is important to ensure that the LOHC molecules still have a high hydrogen storage capacity and can be produced at low cost. To achieve this goal the structure of biological cofactors, e.g. heteroatom insertion, PCET-capable ligand frameworks, and controlled aromaticity, need to be transferred to the yet used molecules for chemical hydrogen storage to reduce dehydrogenation barriers.

We propose the following strategies to optimize heterogeneous catalysts used for LOHC technologies using biological principles: First, the microenvironment of the active-site can be tailored via ligands, supports or porous frameworks to emulate enzymatic protection and transition-state stabilization. This might change the concentration of the reactants at the active site and thus enable reactions, which would not be possible under the process conditions of the bulk. A similar effect can be achieved by implementing redox mediators or structured electron-relay networks to lower effective catalytic overpotentials. This might be achieved by using single-atom catalysts, bimetallic systems and dynamically adaptive catalysts. Another interesting pathway is to explore hybrid systems where hydrogenases or hydrogenase-inspired catalysts are combined with LOHC substrates in electrochemical or

bio-electrochemical configurations. In a next step, the improved activity and selectivity at milder reaction conditions needs to be transferred to a continuous process and the expected benefits need to be demonstrated by rigorous balancing of mass and enthalpy flows over extended operation times.

Ultimately, the convergence of LOHC chemistry with biological and bio-inspired approaches may contribute to a hydrogen economy that is not only technically feasible and efficient, but also more compatible with sustainability and environmental goals: reduced dependence on scarce precious metals, lower energy penalties for dehydrogenation due to improved heat integration, improved cycle life, and improved ecotoxicological profiles of LOHC molecules. Importantly, biology illustrates that hydrogen can also be stored indirectly yet very stably in carbon–carbon bonds via central metabolites and long-term reservoirs such as lipids, polyhydroxyalkanoates or carbohydrates. These reservoirs represent dense, robust forms of "hydrogen-equivalent" storage that emerge from enzymatically controlled redox conversions at near-ambient conditions. Incorporating analogous design principles - high selectivity, modular redox coupling, and efficient regeneration - into LOHC systems and hybrid catalytic architectures may ultimately broaden the palette of reversible hydrogen carriers and create new synergies between molecular hydrogen storage and carbon-based energy vectors in a circular, low-carbon energy system.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the authors used ChatGPT in order to edit the language. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Peter Wasserscheid reports a relationship with Hydrogenious LOHC Technologies GmbH, Erlangen that includes: equity or stocks. The other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Abbreviations

1,3-BPG	1,3-bisphosphoglycerate
acetyl-CoA	Acetyl-coenzyme A
AcP	Acetyl Phosphate
ATP	Adenosine Triphosphate
CAPEX	Capital Expenditure
DFT	Density Functional Theory
F_{420}	Coenzyme F_{420}
FAD	Flavin Adenine Dinucleotide
Fdx	Ferredoxin
FMN	Flavin Mononucleotide
H0-NEC	N-ethylcarbazole
H12-NEC	perhydro N-ethylcarbazole
H0-DBT	Dibenzyltoluene
H18-DBT	perhydro-Dibenzyltoluene
LOHC	Liquid Organic Hydrogen Carrier
NAD(P)	Nicotinamide Adenine Dinucleotide (Phosphate)
OPEX	Operating Expenditure
PCET	Proton-coupled Electron Transfer
PEP	Phosphoenolpyruvate

Data availability

Data will be made available on request.

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