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हाइड्रोजन भंडारण अनुप्रयोगों के लिए ठोस-अवस्था पदार्थों की वर्तमान प्रगति और भावी दृष्टिकोण

Current Progress and Future Perspectives of Solid-state Materials for Hydrogen Storage Applications

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सारांश

ठोस-अवस्था हाइड्रोजन भंडारण में धातु हाइड्राइड, उच्च पृष्ठीय क्षेत्रफल वाले मैट्रिक्स तथा रासायनिक/कॉम्प्लेक्स हाइड्राइड जैसे पदार्थों का उपयोग हाइड्रोजन को सुरक्षित रूप से उच्च घनत्व और अपेक्षाकृत कम दाब पर अवशोषित एवं संग्रहीत करने के लिए किया जाता है। यह पारंपरिक हाइड्रोजन भंडारण प्रणालियों से संबंधित आयतन तथा सुरक्षा संबंधी समस्याओं का समाधान करता है, जिससे यह स्थिर विद्युत आपूर्ति, विद्युत ग्रिड के लोड संतुलन तथा शून्य-उत्सर्जन वाहनों के लिए एक उपयुक्त विकल्प बनता है। प्रस्तुत लेख में ठोस-अवस्था हाइड्रोजन भंडारण के लिए विभिन्न संभावित पदार्थों तथा रासायनिकी वर्ग में चल रहे संबंधित अनुसंधान कार्यों पर चर्चा की गई है।

ABSTRACT

Solid-state hydrogen storage uses materials like metal hydrides, high surface area matrix and chemical/complex hydrides to safely bind and store hydrogen at high densities and lower pressures. It resolves the volume and safety issues of conventional storage, making it ideal for stationary power, grid balancing, and zero-emission vehicles. In the present article different candidate materials for solid state hydrogen storage and the on-going research in Chemistry Group are discussed.

KEYWORDS: Hydrogen storage materials, Metal Hydrides



धातु हाइड्राइड के रूप में हाइड्रोजन भंडारण-मिश्रधातु।

Hydrogen Storage in the form of metal hydride

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Introduction

Solid state hydrogen storage materials are solid substances that can absorb, bind, or react with hydrogen to store it safely and efficiently with high densities [1]. They provide a compact, low-pressure alternative to conventional hydrogen storage methods such as compressed hydrogen gas or cryogenic liquid hydrogen, which is critical for making hydrogen fuel viable for vehicular applications and clean energy grids. Storing hydrogen in its pure form presents severe physical challenges. Storage in high pressure cylinder requires extreme pressures (up to 700 bar), which demands heavy, expensive, and potentially hazardous cylindrical tanks. Hydrogen stored in the liquid form requires cryogenic cooling to -253°C , consuming massive amounts of energy just to maintain the temperature. More conveniently, solid state hydrogen storage materials pack hydrogen atoms or molecules closely together inside a solid matrix by chemical or physical interaction, allowing high volumetric density at or near room temperature and ambient pressure. Extensive research is being pursued in the attempt to develop cost effective hydrogen storage materials with high storage capacity, favourable thermodynamics and kinetics for hydrogen charging-discharging and good cyclic stability for both heavy duty vehicle and stationary applications such as heat storage, heat pump, air conditioning of building etc. However, due to practical consideration regarding gravimetric storage capacity at ambient temperature and pressure, the use of solid state hydrogen for vehicular application poses the most demanding challenges for onboard hydrogen storage and delivery. Comparatively lower hydrogen storage capacities can be accepted for stationary applications as weight and volume are not limiting factors in this case.

The hydrogen storage properties of different types of solid state materials have been explored extensively worldwide

and are summarized in Table-1. The various solid state hydrogen storage materials have their own merits and limitation and some of them show very high capacity, fast kinetics, but poor reversibility, again few materials show excellent reversibility suitable condition of operation, but comparatively poor hydrogen uptake. Various factors responsible for this are binding energy, storage mechanism and types of interaction among hydrogen and storage matrix. Depending on that solid state hydrogen storage materials are broadly classified into three categories.

Physical Adsorption on Solid State Materials (Physisorption)

Porous, high-surface-area materials bind hydrogen molecules (H_2) weakly to their surfaces through Van der Waals forces. Key examples are carbon nanotubes (CNTs), graphene oxide, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs) (Fig.1). They are characterised by their fast absorption and desorption cycles, and good cyclic stability, but typically require cryogenic temperatures -196°C to store substantial amounts of hydrogen. Several works have been carried out both theoretically and experimentally in Chemistry Group, BARC, to optimize the interaction energy of hydrogen with the carbon-based materials by modifying low-dimensional nanostructured carbons (such as carbon nanotubes and graphene oxide) to overcome their weak ambient-temperature hydrogen affinity and to maximize storage capacity and stability. Functionalized graphene oxide and heterostructures addresses the poor ambient-condition performance of conventional carbon frameworks by incorporating advanced chemical modifications. Our recent research found that, the use of unconventional highly functionalized graphene oxide (HGO), instead of standard graphene oxide (GO), increases the surface functional group density tremendously, which allows a vastly superior distribution and higher loading of palladium (Pd)



Table-1: Hydrogen storage performance comparison of various solid state hydrogen storage materials.

Sr. No	Material Class	Capacity (wt.%)	Storage mechanism	Kinetics	Operating Temperature	Reversibility	Examples	Technology Maturity	Ref.
1	Carbon based materials	1-7	Physisorption	Excellent	Very low	Excellent	CNTs, graphene	Medium	2
2	Chemical Hydrides	8-20	Covalent bonding	Good	Medium	Poor	NH_3BH_3 , NaBH_4	Medium	3
3	Porous materials	1-10	Physisorption	Excellent	low	Excellent	MOF-5, COF-1	Medium	4
4	HEA Hydrides	1-3.8	Chemisorption	Good	Medium	Good	Ti-Zr-Sc-Cr-V-Ni	Emerging	5
5	Complex Hydrides	5-18	Ionic-Covalent bonding	Moderate	Medium-high	Poor	NaAlH_4 , LiAlH_4	Medium	3
6	Intermetallic Hydrides	1-4.0	Chemisorption	Excellent	Medium	Good	LaNi_5 , Ti-Cr-V	High	13
7	Mg-based Hydrides	5-7.6	Chemisorption	Poor	High	Moderate	MgH_2 , Mg_2NiH_4	High	17



nanoparticles across the sheets, enabling enhanced hydrogen adsorption of 6.62 wt.% with reversibility and excellent retention capacity [6]. Apart from that the heterostructure composed of MXene-graphene oxide combines the high surface area of graphene with the catalytic metallic nature of MXenes creates a synergistic effect that boosts total gas absorption capacity establishing a total capacity of 5.26 wt.% at 173 K [7]. CNT architectures optimisation is carried out by *ex-situ* metal doping, to trigger the “hydrogen spillover” effect—where molecular hydrogen dissociates on a metal catalyst and migrates onto a carbon support. Our research showed that the finely dispersed 3–5 nm size Pd nanoparticles interact directly with the CNT support, enhancing the hydrogen spillover efficiency [8]. Even the synthesis method plays a very important role towards the enhancement of the spillover effect. Comparative evaluations of wet impregnation, polyol methods and reverse micellar route for dispersion of Pd nanoparticle on CNT support showed that the reverse micellar pathway achieves the most stable and uniform dispersion [9]. Apart from the metal doping, in-situ non-metal doping also plays major role towards the hydrogen storage in CNT. Chemical alterations via boron and nitrogen co-doped carbon nanotubes, chemically polarize the carbon lattice, making it more favorable for hydrogen molecules to bind at ambient conditions. Our study showed that the BCNT-based systems can achieve capacities of 2.5 wt.% at 77 K through localized dipoles created by 3.86 at % boron substitution. Structural evolution of porous and turbostratic carbons showed that the structural disorder and geometry of the pure carbons dictate the gas absorption capacity [10] and the chaotic misorientation of carbon layers influence localized hydrogen storage parameters. DFT modeling of carbon-like nanostructures are also considered as a very useful tool for optimisation of the hydrogen storage

properties. Using computational plane-wave pseudopotential methods, the binding mechanism of hydrogen with titanium-decorated silicon carbide (SiC) sheets and (10,0) single-walled SiC nanotubes was established. The DFT calculations demonstrated that titanium decoration distorts the atomic grid of SiC, allowing each Ti metal atom to bind up to four hydrogen molecules with an optimal, reversible average binding energy of 0.37 to 0.65 eV [11].

Metal Hydrides

Certain metals or alloys react chemically with hydrogen, breaking the H_2 molecule apart and storing individual hydrogen atoms within the interstitial spaces of the metal's crystal lattice. Key examples are MgH_2 , $LaNi_5$, TiFe, and body-centered cubic (BCC) alloys. Metallic hydrides are exceptionally safe and possess high volumetric storage capacity at room temperature and ambient pressure. However, they are often heavy and require high temperatures to release the trapped hydrogen. The research on metal hydrides and solid-state storage alloys in Chemistry Group, BARC focuses heavily on engineering multi-component alloy systems to operate under optimal thermodynamic and kinetic windows. The major research approaches targets specific pitfalls of raw metal hydrides like severe thermodynamic stability (requiring excessive release temperatures) and sluggish, multi-stage absorption/desorption kinetics. Among different metal hydride systems, advanced Ti-Cr-V based body-centered cubic (BCC) alloys were found to be highly promising, because they achieved high volumetric storage capacities (~4 wt%) at moderate temperature and pressure (Fig. 2). Modifications of their internal chemical compositions fine-tune their hydrogen storage properties. Zr Substitution for Ti in

$Ti_{0.43}Zr_{0.07}Cr_{0.25}V_{0.25}$ alloy demonstrated that substituting titanium with zirconium drops the hydride desorption temperature by roughly 50 K. This indicated a substantial lowering of the system's overall thermodynamic stability, making hydrogen extraction significantly easier [12]. The inclusion of secondary Laves phases alongside the main BCC matrix also altered hydrogen storage properties. The phase configuration acted as a kinetic highway, allowing fast hydrogen capture without requiring prolonged initial activation cycles. Transition metal doping in $Ti_{2x}CrVM_x$ ($x = Fe, Co, Ni$) alloys showed that the addition of elements like nickel or iron weakened localized metal-hydrogen binding, preventing the framework from locking up the hydrogen permanently [13]. The substitution behavior of iron, vanadium, and zirconium within $LaNi_5$ -type classical alloys showed that the vanadium-substituted formulations $LaNi_4V_{0.5}Fe_{0.5}$ created flat, highly reproducible pressure-composition-temperature (PCT) isotherm plateaus near 1 bar at room temperature, required for room-temperature operational capability. This makes it perfectly balanced for commercial distribution systems, whereas zirconium substitution results in uneven, sloped operational pressures [14]. While magnesium hydrides, MgH_2 , have high storage capabilities by weight (7.6 wt.%), they typically require operational temperatures exceeding 300°C. Density Functional Theory (DFT) modeling and experimental surface studies showed that the transition metal catalysis like Ti, V, and Ni modulate the dissociation and diffusion kinetics of

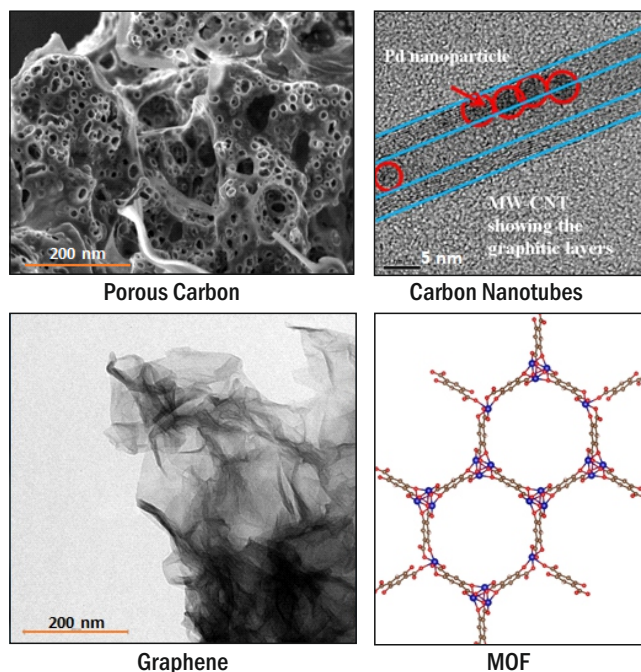
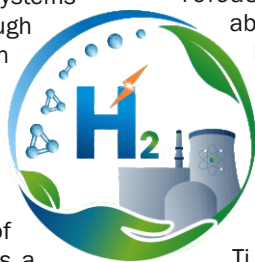


Fig.1: Different classes of materials for hydrogen storage by physisorption.

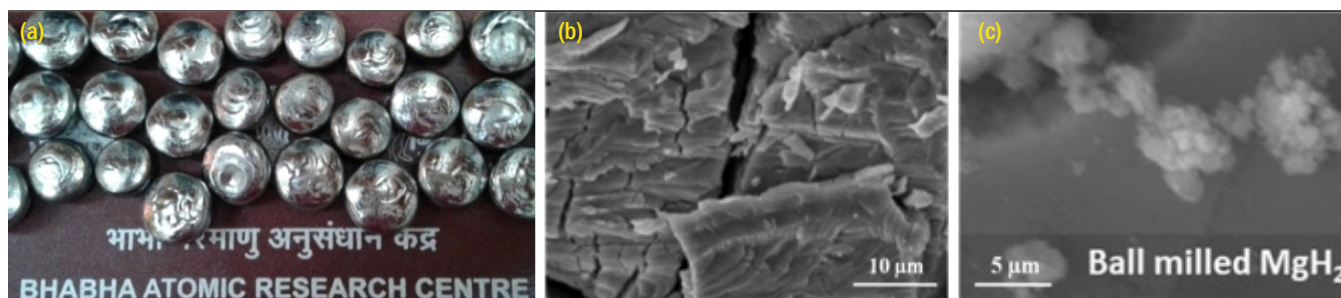


Fig.2: Hydrogen Storage in the form of metal hydride (a) Alloy (b) Scanning Electron Microscopy of pulverised metal hydride (c) Ball milled magnesium hydride.

hydrogen on Mg(0001) surface [15]. Theoretical calculation proved that placing transition metals on the surface or subsurface layers dramatically lowers the energy barriers required to split the H₂ molecule apart. Modeled small Ti-doped magnesium clusters TiMg₅₄ and TiMg₈ showed that structural scaling down to the nanoscale alters the electron density, which forces immediate molecular dissociation and atomic diffusion into the internal storage sites at much lower thermal inputs [16]. Detailed hydriding mechanism and kinetics analysis study in the engineer scaled storage reactors, maps out exactly how hydrogen travels into bulk metals. Using standard kinetic fitting equations on experimental data showed that hydrogen atoms after dissociation on the surface travel inside the engineered nano-magnesium and are bounded first by random atomic nucleation, followed by 1D and 3D diffusion through the formation of hydride surface layer [17].

Chemical and Complex Hydrides

Chemical and complex hydrides represent a major class of solid-state hydrogen storage materials capable of binding hydrogen via strong covalent or ionic chemical bonds. Unlike physical adsorption materials, that require cryogenic temperatures, these hydrides achieve exceptionally high volumetric and gravimetric hydrogen densities at or near ambient conditions. Major classes of complex hydrides feature a central metal or non-metal atom covalently bound to hydrogen, forming a complex anion paired with a light metal cation: Sodium borohydride (NaBH₄) and Lithium borohydride (LiBH₄) boast immense theoretical hydrogen storage capacities. Hydrogen release from air-stable NaBH₄ is typically triggered via catalytic hydrolysis. Sodium alanate (NaAlH₄) is the most widely studied complex hydride. It releases hydrogen in a multi-step thermal decomposition path. Doping it with titanium (Ti) catalysts makes the reaction reversible under practical conditions. Systems like Lithium amide (LiNH₂) store up to (6.5 wt.%) hydrogen, when reacted with lithium hydride (LiH). They function via a reversible amide-to-imide phase transformation pathway. Chemical hydrides store hydrogen within molecular compounds and release it through a breakdown of their primary chemical structure. Ammonia Borane (NH₃BH₃, AB) contains both hydridic (B–H) and protonic (N–H) hydrogens, creating a high-density molecular crystal (19.6 wt.% hydrogen). It releases hydrogen at low temperatures via catalytic hydrolysis or at high temperature by stepped thermal decomposition.



The research on ammonia borane (NH₃BH₃, AB) in Chemistry Group, BARC centers around the development of highly efficient, recyclable catalysts (Fig.3) to unlock its massive theoretical hydrogen storage capacity (19.6 wt.%). Ammonia borane suffers from sluggish hydrogen release at room temperature and generates volatile impurities like ammonia (NH₃) gas; as a result the research work mainly focuses on catalytic hydrolysis to ensure safe, room-temperature green hydrogen production. Designing specialized support matrices to highly disperse metal nanoparticles, lowers the activation energy (E_a) required for snapping the molecular bonds of AB. A green synthesis method using electron beam irradiation was developed, to decorate palladium nanoparticles (<10 nm) on a graphitic carbon nitride matrix demonstrating that the catalyst slashed the hydrolysis activation energy to an impressively low (27.36 kJ mol⁻¹) [18]. Biomass-derived cost-effective, porous carbon supported palladium nanoparticles, yielded a 3.4-fold reduction in activation energy compared to uncatalyzed AB hydrolysis [19]. Engineered magnetically separable copper-iron oxide polymer beads (Cu@Fe₃O₄:PES) provided a scalable, non-noble metal alternative for rapid hydrogen evolution from AB [20]. A major challenge with ammonia borane hydrolysis is the co-release of trace ammonia gas, which can poison fuel cell membranes. Recent work on pore-engineered, non-noble metal ZIF-67 (Zeolitic Imidazole Frameworks) acted as a dual-function matrix, which catalyzed the hydrogen generation reaction showing remarkably low activation energy of 15.63 kJ mol⁻¹, while chemically trapping and mitigating released ammonia [21]. Pd-dispersed MOFs were also developed, that enable ammonia-free hydrogen generation from both ammonia borane and sodium borohydride in aqueous solutions [22]. To completely avoid reliance on metal based catalysts, use of macrocyclic “nanocavitands” was established to structurally manipulate the AB molecule, demonstrating a metal-free supramolecular strategy, where cucurbit[5/8]uril nanocavitands encapsulate ammonia borane. This lowered the hydrolysis activation energy from 103.8 kJ mol⁻¹ down to 27.5 kJ mol⁻¹, matching the performance of expensive platinum and palladium metal nanoparticles—while significantly suppressing unwanted volatile ammonia release [23]. Utilizing time-dependent FT-IR and mass spectrometry study coupled with Kinetic Isotope Effects (KIE) proved that the evolved hydrogen gas originating from a synchronized splitting of both

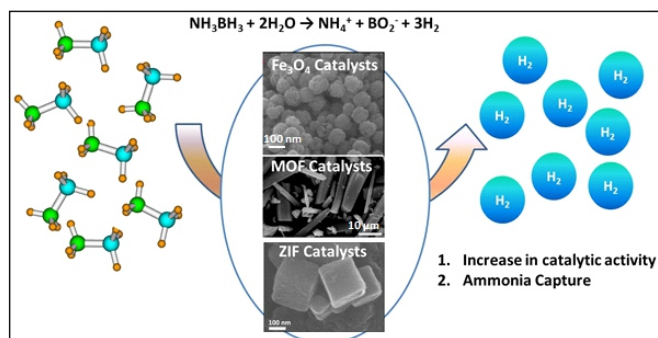


Fig.3: Room temperature hydrogen release from ammonia borane in presence of different catalysts.

the internal (B–H) bonds of ammonia borane and the (O–H) bonds of the surrounding water solvent.

Way forwards

Recent research on hydrogen storage is shifting from heavy, rare earth metal hydrides to lightweight alternatives such as vanadium-based, magnesium-based alloys and light element based complex frameworks. These allow for higher hydrogen storage capacities and faster absorption/desorption rates at near-ambient temperatures. To solve the challenge of transporting compressed or cryogenic hydrogen, developers are testing solid-state hydrogen storage technologies (like hydrogen-rich powders) that can be easily transported at low pressures and later processed to release clean fuel. To become viable for mainstream automotive and stationary applications, storage materials are required to hit specific targets, including a cost-effective production benchmark, moderate operating temperatures, and a maximum hydrogen weight percentage. While long-term adoption aims to fuel zero-emission vehicles, the immediate way forward focuses on stationary energy storage, remote off-grid community power, and microgrids where the safety and compact footprint of solid-state hydrogen storage systems outweigh traditional high-pressure tanks.

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