Sanvahak (संवाहक)

An International Peer Reviewed, Refereed, Indexed, Multidisciplinary (All Discipline/Subjects), Multilingual (All Languages) & Quarterly Research journal

ISSN : 3108-1347 (Online)

IIFS Impact Factor-5.25

Vol.-2; Issue-3 (July-Sept.) 2026

Page No.- 01-13

https:// sanvahak.gyanvividha.com

Author's:

1. Kundan kumar singh
Research scholar - physics department, NIILM university kaithal Haryana.

2. Dr. hitesh kumar
Research supervisor - professor physics department, NIILM university Kaithal, Haryana.

Corresponding Author :

Kundan kumar singh
Research scholar - physics department, NIILM university kaithal Haryana.

A Comparative Density Functional Theory Study of Hydrogen Storage in Graphene, Borophene and MXene Nanomaterials

Abstract : Although hydrogen is generally considered to be an ideal energy carrier for a post-fossil fuel economy, the most significant drawback in large-scale utilisation is the lack of a lightweight, safe and reversible storage medium, especially for mobile applications. Two-dimensional (2D) nanomaterials are attractive for solid-state hydrogen storage due to their extremely high surface area and tunable electronic structure and potential for chemical functionalisation. In this review, the density functional theory (DFT) studies of hydrogen adsorption are summarised and critically compared on three representative 2D platforms, namely, graphene, borophene and MXenes. For all three materials, the surface of a pristine sheet interacts with molecular hydrogen only via weak Van der Waals physisorption (with binding energies below 0.1 eV per H2), which is not enough for effective reversible storage at ambient conditions. New DFT calculations for dozens of independent systems demonstrate that decoration with alkali metals (Li, Na, K) and early transition metals (Sc, Ti, V, Zr) polarises the host lattice, increases per H2 binding energies within the 0.1-0.5 eV range proposed for reversible operation near ambient temperature, and supports Kubas-type orbital interactions. The gravimetric capacities range from below 1 wt% for clean sheets to over 13 wt% for optimally decorated borophene, well above the 2025 ultimate target of the United States Department of Energy (DOE) of 6.5 wt%. The review provides a tabulation and graphical comparison of the exchange correlation functionals, dispersion corrections, and adsorption energies reported in the literature, gravimetric densities and desorption temperatures, as well as a discussion on the structural, electronic and thermodynamic factors that distinguish the three material families. The

challenges of metal clustering, moisture and oxidation sensitivity, synthesis of single-phase borophene at scale, and the limitations of conventional exchange-correlation functionals for studying weak interactions are summarised, and plans for using machine learning-accelerated DFT screening and experimental testing are proposed.

Keywords : Density Functional Theory; Hydrogen Storage; Graphene; Borophene; MXene; 2D Nanomaterials; Physisorption; Metal Decoration; Gravimetric Capacity; Renewable Energy.

1. Introduction : One of the most promising pathways towards deep decarbonisation of the transport, industrial and power-generation sectors is the shift away from carbon-intensive fuels towards a hydrogen-based energy economy. Hydrogen has the highest gravimetric energy density of any chemical fuel (approximately 120-142 MJ per kg), and on oxidation in a fuel cell it produces nothing more than water, and in theory is renewable by electrolysis of water (Martins, 2024). These benefits do not prevent hydrogen from being a significant engineering challenge for efficient, safe and convenient storage, however, because the volumetric energy density of hydrogen under ambient conditions is very low, and efficient, safe and compact storage is the critical engineering challenge between hydrogen production and widespread end use, particularly in light-duty vehicles and portable devices (Mishra, 2024). The conventional storage methods, including high-pressure compression (35-70MPa) and cryogenic liquefaction (20K), are energy-consuming and involve the use of heavy or thermally insulated tanks, and safety issues are well documented. A more compact and safer alternative is solid-state storage, where the hydrogen is trapped within a host material and can be extracted when needed by small changes in temperature and/or pressure. Work on various solid-state hosts, including metal hydrides, complex hydrides and porous frameworks like metal-organic frameworks (MOFs) and zeolites, has been undertaken, but so far gravimetric capacity, reaction speed, cost or operating temperature has been limiting for commercial use at the scale needed for transport applications (Jayan, 2026).

The two-dimensional nanomaterials have been the subject of high research interest as hydrogen storage media in the past 20 years due to their atomically thin, high surface area structure that exposes a very large fraction of the surface atoms, and due to the systematic modification of surface chemistry via creating defects, adatoms and doping. After the experimental isolation of graphene, the archetypal 2D material made of sp2-hybridised carbon in a honeycomb lattice, it was the first material to be studied in detail for hydrogen uptake (Ajmal, 2025). Borophene - a single-atom thick sheet of boron atoms that were first synthesized on a silver surface in 2015 - and MXenes - a family of two-dimensional transition-metal carbides, nitrides and carbonitrides produced by selective etching of MAX phases - were suggested as alternative or complementary materials to graphene, owing to the electron deficiency of boron, which promotes strong adsorption of molecules, and to the tunable terminations and metallic conductivity of MXenes. Due to the high cost and time required to test the adsorption energy, optimal binding configuration, change in electronic structure and thermodynamic storage parameters of adatoms as they are directly synthesised in a given composition/structure, density functional theory (DFT) is now the workhorse computational approach to predict these before the experimental synthesis. In the case of graphene, borophene and MXene based hydrogen storage systems, there has been a proliferation of DFT literature recently, but many of the studies are independent, with variations in exchange-correlation functional, dispersion correction scheme, and decorating species and reported figures of merit, making systematic comparison across materials difficult for beginners to the field (Bilgiç, 2024).

This review paper aims to fill this gap by (i) summarizing the necessary DFT

methodology applied in the analyzed literature, (ii) critically reviewing and tabulating the hydrogen adsorption results for pristine, defect-engineered and metal-decorated graphene, borophene and MXene systems, (iii) comparing the gravimetric capacity, binding energy and desorption temperature of these 2D platforms with the benchmarks established by the United States Department of Energy (DOE) and (iv) highlighting the outstanding scientific and engineering challenges that need to be overcome for any of these 2D systems to be deployed for use in practical onboard hydrogen storage.

2. Density Functional Theory Framework and Computational Considerations : The many-body Schrödinger equation for interacting electrons is transformed into a set of single-particle equations called the Kohn-Sham equations, which are based on the electron density instead of the many-body wavefunction, allowing first-principles calculation of total energies, geometries and electronic structure to be accomplished for systems comprising hundreds of atoms. All the hydrogen storage studies reviewed here use a periodic plane-wave or localised-basis-set DFT code (e.g., VASP, Quantum ESPRESSO, CASTEP, SIESTA) with the GGA, in the current case the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, and with the core electrons described by projector-augmented-wave (PAW) or ultrasoft pseudopotentials (Ghotia, 2025). One of the key methodological challenges in this area is that the van der Waals dispersion forces that arise between the molecular hydrogen and the pristine 2D sheet dominate the weak physisorption interaction, and are not incorporated in standard local and semi-local exchange-correlation functionals (Yadav, 2022). This implies that, for essentially all quantitatively reliable studies, an empirical or semi-empirical dispersion correction is included, most often the Grimme DFT-D2 or DFT-D3 schemes or the Tkatchenko-Scheffler method, to calculate a physically meaningful H2 binding energy; otherwise the H2 adsorption minimum on pristine graphene, borophene and MXene surfaces is systematically underbound (or even missed).

The adsorption or binding energy is, conventionally, Eb = E(host+nH2) - E(host) - nE(H2) / n, where E(host+nH2), E(host) and E(H2) are the total energies of the hydrogen loaded system, the bare host and an isolated hydrogen molecule, respectively; and a negative value corresponds to a thermodynamically favourable, exothermic adsorption process (Wang, 2025). The gravimetric hydrogen storage capacity is the mass of hydrogen adsorbed to the total mass of the hydrogen-loaded system, typically reported in weight percentage (wt%). The ab initio molecular dynamics (AIMD) simulations at finite temperature are often used as a complementary test of the thermal and structural stability, and the estimated desorption temperatures are obtained from the binding energies calculated by the ab initio simulations using the van't Hoff equation or a simplified quasi-harmonic approximation, with the appropriate pressures for on-board fuel-cell operation (Gupta, 2025).

The main computational parameters- exchange-correlation functional, dispersion scheme, pseudopotential type/simulation code- reported in a representative sample of the graphene, borophene and MXene hydrogen storage studies reviewed in this work are summarised in Table 1, highlighting the convergence of the methods and some remaining diversity in the field.

Table 1. Representative computational parameters used in DFT studies of hydrogen storage on graphene, borophene and MXene surfaces

Study / System	DFT Code	XC Functional	Dispersion Correction	Basis / Pseudopotential
B/V-doped porous graphene	VASP	GGA-PBE	DFT-D3	PAW

Li-N co-doped graphene (BC4N)	Quantum ESPRESSO	GGA-PBE	DFT-D2	Ultrasoft pseudopotential
Sc-decorated Ψ-graphene	VASP	GGA-PBE	DFT-D3 (Grimme)	PAW
TM-modified B-doped graphene	CASTEP	GGA-PBE	Not specified (US pseudopotential)	Ultrasoft, plane-wave (500 eV cutoff)
Li/Na/Ca-decorated borophene	Quantum ESPRESSO	GGA-PBE	DFT-D (Grimme)	Vanderbilt ultrasoft
Li-decorated bilayer borophene	VASP	GGA-PBE	DFT-D3	PAW
Li/Na/K-decorated B_2O	VASP	GGA-PBE	DFT-D2	PAW
Sc_2N MXene	VASP	GGA-PBE	DFT-D3	PAW
Multilayer $Ti_3C_2T_x$ MXene	VASP / Quantum-thermodynamic model	GGA-PBE	DFT-D2	PAW
Li-decorated Ti_2CF_2 MXene	VASP	GGA-PBE	DFT-D3	PAW

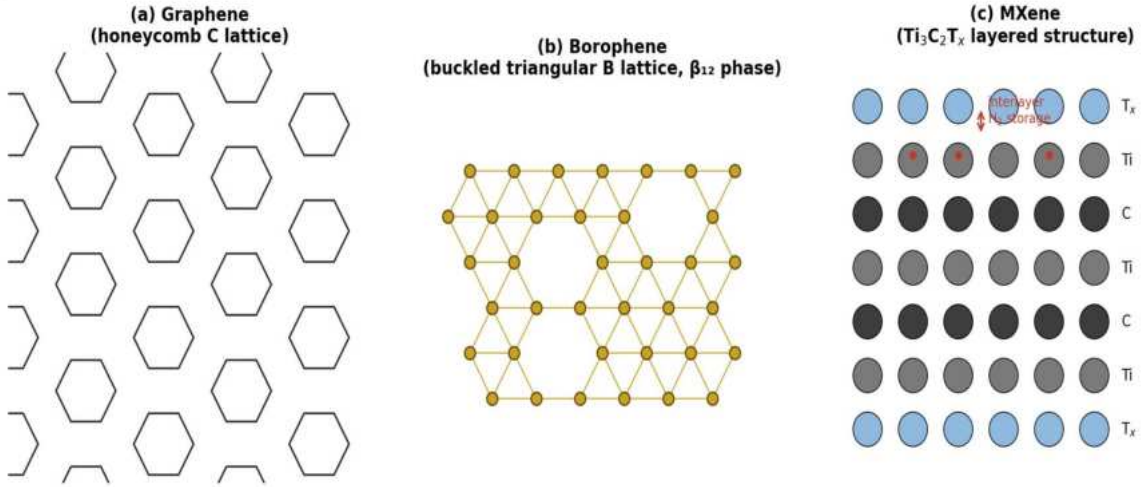

Figure 1. Schematic representation of the three two-dimensional host lattices reviewed in this paper: (a) the honeycomb sp2 carbon lattice of graphene, (b) the buckled triangular boron lattice with periodic hexagonal vacancies characteristic of the β12 borophene polymorph, and (c) the layered Mn+1XnTx architecture of Ti3C2Tx MXene, showing surface terminations (Tx) and the interlayer gallery available for hydrogen storage.

3. Hydrogen Storage in Graphene-Based Nanomaterials

3.1 Pristine and Defect-Engineered Graphene : The potential to store hydrogen in graphene is initially promising due to its single-atom-thick, honeycomb lattice that has a theoretical specific surface area of approximately 2630 m2/g, the highest of any carbon allotrope. The molecular hydrogen, however, has been shown to interact with pristine graphene by weak, non-directional

van der Waals physisorption, with the binding energy typically found in the range 0.03-0.08 eV per H2, which is below the range of 0.1-0.4 eV that is generally considered necessary for hydrogen to be held at near-ambient temperature while being desorbed under a practical swing of pressure (Joseph, 2020). In this context, it is clear that, in its pristine form, graphene alone does not exhibit technologically relevant hydrogen storage capacities at room temperature, and almost all of the subsequent DFT studies on hydrogen storage capacities on graphene have centred on ways to increase the inherent graphene-H2 interaction (Bakhit, 2023).

Stone-Wales defects, heteroatom doping (boron, nitrogen, phosphorus), and the introduction of vacancies into the graphene lattice that change the local electronic structure can moderately increase the hydrogen binding energy by the formation of a locally polarised or under-coordinated carbon site. It is especially widely adopted as a precursor step before metal decoration, as the electron-deficient character it creates strengthens the binding of the alkali or transition-metal adatoms that follow, thus determining the subsequent H2 adsorption strength. Adding periodic sub-nanometre pores makes porous graphene variants that offer extra low-coordination sites to further stabilise metal decoration and increase the effective surface area available for hydrogen uptake (Bakhit, 2024).

3.2 Metal-Decorated Graphene: Alkali and Alkaline-Earth Metals : Graphene lithium decoration has been investigated the most, mainly because Li is the lightest alkali metal, and hence the gravimetric loss when calculating storage capacity is the least. The DFT studies of Li-decorated porous and nitrogen-doped graphene show that the maximum gravimetric capacity is as high as 8.8 wt%, with average binding energies of about 0.12 eV per H2 molecule, surpassing the ultimate target set by DOE. Charge-transfer analyses (Bader and Mulliken population analysis) always indicate that the Li atoms lose electron density to the graphene sheet and become partially cationic (Li-delta+), while the polarised electric field of the H2 molecule favours an attractive charge-quadrupole interaction which is complementary to the van der Waals attraction (Macilon, 2025).

One design principle that emerged from a review of this literature is the avoidance of the formation of metal-metal clusters: The cohesive energy of bulk lithium (and most alkali and transition metals) is similar to or higher than the metal-graphene binding energy, which means that adatoms that are not decorated at a high areal density, or on an unfavourable substrate, tend to clump together into clusters that resemble bulk metal and thus do not possess the enhanced hydrogen-binding capacity (Ibrahim, 2022). Methods of increasing the metal-substrate binding energy beyond the competing cohesive energy include: vacancy engineering, choice of low coordination porous sites, and substitution doping (B, N). All of these methods have been reported to increase the metal-substrate binding energy above the competing cohesive energy, kinetically and thermodynamically suppressing clustering.

3.3 Metal-Decorated Graphene: Transition Metals : Transition metal decoration (usually Sc, Ti, V and Zr) typically results in the formation of stronger, partly covalent metal-hydrogen interactions via the Kubas mechanism, which involves the filled H-H sigma bonding orbital donating electron density to the empty metal d-orbital and the metal in turn donating electron density to the H2 sigma-antibonding orbital, which weakens the H-H bond without destroying it. The interaction is generally of dual-channel nature; the binding energy is in the range 0.3-0.65 eV/H2, which is within the ideal reversible-storage window, and each transition-metal centre can coordinate more than one H2 molecule in a non-dissociative molecular fashion. The representative results are Ti-functionalised graphene with a gravimetric density of 7.8 wt%, with an average binding energy of 0.35 eV per H2, Zr-decorated graphene with 11 wt%, with nine H2

molecules bound per Zr centre at an average binding energy of 0.34 eV per H2 and Sc-functionalised Psi-graphene, a graphene allotrope containing four-, six- and eight-membered rings, with an uptake exceeding 11 wt% at a desorption temperature near 400-410 K, well suited for fuel-cell operating conditions (Pal, 2024).

Boron-doping and decoration of the B with transition metals results in an additional synergistic effect: DFT calculations of the metal binding energies of the B decorated with Sc, Ti and V show a 1.7-1.9 eV enhancement relative to undoped graphene, with each of the three systems shown to have a stable adsorption of 4-5 H2 molecules, with adsorption energies of ~-0.53 to -0.65 eV per H2 and where the B decorated with Sc was identified as the best performing configuration among the three transition metals studied. Decoys with palladium clusters on vacancy-engineered graphene have also been investigated for their high H2 binding strength (approx. -5.4 eV for the Pd4 cluster), but the formation of the hydride-like Pd-H bond may be so strong that full reversibility is hard to achieve without another spillover or thermal-swing mechanism (Alikhani, 2024).

4. Hydrogen Storage in Borophene-Based Nanomaterials

4.1 Structural Polymorphism of Borophene : Elemental boron does not form a single unique 2D allotrope, unlike graphene. Boron is one electron shorter than carbon, so the ideal structure of boron is an electron-deficient triangular lattice, which was instead found in the experimentally and theoretically more stable borophene phases, such as those with periodic hexagonal vacancies, such as the beta12 and chi3 phases grown on Ag(111) substrates in 2015, that partially compensate for the electron deficiency (Makaremi, 2018). This structural flexibility leads to an anisotropic surface morphology of borophene, which is corrugated and contains several distinct adsorption sites (hollow, bridge, and vacancy-centre sites) not found on the uniform surface of graphene, and is a key factor in the intrinsically different reactivity of borophene toward adsorbates and dopants compared to its carbon-based 2D counterparts.

4.2 Pristine Borophene and the Physisorption Baseline : For the pristine sheet, DFT calculations converge towards a very weak interaction between the H2 molecule and the surface, reported as a binding energy of ~ -0.045 eV per H2, which is similar (but slightly larger) than the binding energy of hydrogen physisorbed above pristine graphene. This weak baseline interaction is not enough for practical storage – as is the case with graphene – and is the driving force behind the considerable amount of literature on metal decoration that exists below. One important structural property of borophene that is unique is the presence of intrinsic or engineered vacancy defects, known as double vacancies (DV), which can increase the gravimetric hydrogen density as high as 9.2 wt% even when the surface is not decorated with a metal, because the undercoordinated Bor atoms at a vacancy site bind H2 more strongly than the pristine lattice (Arif, 2025).

4.3 Alkali-Metal- and Alkaline-Earth-Metal-Decorated Borophene : Recently, the decoration of borophene with lithium, sodium and calcium atoms has been the focus of a number of independent investigations of the material using DFT techniques, due to the low mass of boron and its high tendency to electropositive adatoms. Decorated with alkali-metal atoms, the H2 binding energy of pristine borophene is shifted from -0.045 eV per H2 within the reversible-storage window to the range of -0.12 to -0.36 eV per H2, which is still within the desired reversible-storage window. The maximum gravimetric capacities reported for the various decoration patterns studied and borophene polymorphs are also widely differing: single-sided Li decoration of beta12 borophene has been reported to reach a gravimetric density as high as 13.7 wt%, one of the highest reported values for any 2D material in the DFT literature reviewed here,

whileNa- and Ca-decorated borophene have been reported at approximately 9.0 wt% and 7.6-7.2 wt% respectively; double-sided decoration schemes (such as NLi4 superalkali clusters) have been shown to push these capacities to 7.66 wt% and meanwhile push the per-H2 binding energy into more moderate range of values, roughly -0.07 to -0.18 eV per H2, which are more readily reversible (Martins, N. F., Laranjeira, J. A., Lima, 2026).

In addition, just like MXenes (see Section 5), borophene phases with multiple layers or two-layer structures (such as boron hydride (BH) sheets decorated with Li and K) were shown to support stacked H2 adsorption in the interlayer gallery with gravimetric densities of up to 38 wt% for the fully Li-loaded bilayer structure reported, suggesting that interlayer confinement can be used as an extra storage channel, apart from simple surface decoration, for H2 storage on borophene.

4.4 Transition-Metal and Substrate-Activated Borophene : The decoration of borophene with transition metals (TMs) is also reported with good hydrogen storage properties, although not as widely investigated as alkali-metal decoration. Combined DFT and AIMD investigation shows that Cu-activated borophene can promote hydrogen adsorption through dissociative adsorption, enabled by charge donation from the Cu substrate and hybridisation of H-s and B-p and Cu-d electronic states, which results in a relatively high hydrogen gravimetric density of 7.08 wt% and relatively high desorption temperature of 706-749 K, demonstrating strong and catalytically assisted chemisorption rather than the physisorptive type, common for alkali-metal decoration, and Kubas-type (Hussein, 2025). As with all three material families discussed here, the design principle demonstrated by these transition-metal activated systems is that the choice of decorating species can be made to tune the H2 binding mechanism to be either weak physisorption, Kubas-type molecular chemisorption, or full dissociative chemisorption, with each exhibiting a different set of desirable trade-offs involving storage capacity, reversibility and operating temperature (Sura, 2025).

5. Hydrogen Storage in MXene-Based Nanomaterials

5.1 Structure, Composition and Surface Termination Chemistry : MXenes is thus a large and growing family of two-dimensional transition-metal carbides, nitrides and carbonitrides with the general formula $M_{n+1}X_nT_x$, where M represents an early transition metal (Ti, V, Cr, Sc, Mo, etc.), X can be carbon and/or N, n is typically 1 to 4, and Tx denotes the surface terminating groups (commonly –O, –OH, –F or combinations thereof) obtained after selective etching of the parent MAX phase. The tunability in composition and structure (involving dozens of different M elements, tunable layer numbers, and a wide range of possible surface terminations) renders MXenes with a very large design space for hydrogen storage compared to graphene or borophene, and thus DFT screening has been a particularly prominent tool to prioritise the experimental investigation of which MXene compositions are worthy of experimental testing.

5.2 Bare and Surface-Terminated MXenes : Relatively strong intrinsic hydrogen affinity compared with pristine graphene and borophene has been reported in DFT calculations of bare (unfunctionalised) MXene monolayers, such as Ti_2C and Sc_2N, with the reported gravimetric ratio of ~9.0 wt% for Sc_2N and up to 8.6 wt% for Ti_2C, attributed to adsorption at the transition-metal centre sites exposed on the bare MXene surface, where hydrogen atoms bind by chemisorption at hollow (H) sites and hydrogen molecules by Kubas-type interaction at top (T) sites above the metal atoms. The DFT results of realistic mixed-T terminations of $Ti_3C_2T_x$, however, always yield much smaller average H2 adsorption energies (on the order of -0.14 eV per H2), and total surface H2 storage capacities of around 2 wt%, which are comparable to the typical values of metal-organic frameworks, but significantly lower than would be seen with bare

or metal-decorated MXene surfaces (Haldar, 2018).

5.3 Interlayer (Multilayer) Hydrogen Storage: The Nanopump Effect : Interlayer (or multilayer) hydrogen storage is one of the features of the layered MXene architecture that is not foreseen by other known H2 storage methods, and involves H2 molecules that are not adsorbed on the outside basal plane surface but rather reside in the van der Waals gallery between adjacent MXene layers. DFT and coupled quantum-thermodynamic modelling of multilayer Ti3C2Tx predict an upper-bound theoretical gravimetric capacity of ~3.8 wt%, which has been cross-validated with simulated X-ray diffraction patterns of the hydrogen-expanded interlayer spacing, suggesting a pressure- and temperature-dependent gravimetric capacity of ~2.1 wt% at 77 K under 25 MPa external pressure and ~0.67 wt% at 300 K under 25 MPa external pressure. Described as a "nanopump effect", where the adjacent Ti2C-type nanolayers with fluorine functionalised surfaces simultaneously and cooperatively trap H2 molecules by weak chemisorption, this confinement-driven storage has been invoked to help rationalise capacities as high as 10.47 wt% measured at the liquid-nitrogen temperature (77 K) and at 2.5 MPa for Ti3C2Tx, significantly higher than the values predicted for basal-plane physisorption alone and an active field of investigation to explain the detailed mechanism which explains this discrepancy between theory and the highest experimental reports (Ibrahim, M. A., Mahmoud, A. H., Soliman, K. A., Mekhemer, 2022).

5.4 Metal-Decorated MXenes : Like graphene and borophene, the decoration of the MXene surface with light alkali metals is a good idea to increase the hydrogen uptake compared to that of bare and terminated surfaces. Li-decorated Ti2CF2 MXenes are reported by DFT studies to be able to stably host Li atoms on the fluorine-terminated surface without clustering (as confirmed by AIMD simulations at room temperature) with a gravimetric capacity of 3.81 wt% by the reversible physisorption of 26 molecules of H2 per simulation cell. This compares favourably to other higher capacity MXene-based systems (e.g., Y2CCl2 (3.00 wt%) and Y2CF2 (3.42 wt%)), but is lower than a number of other systems (e.g., Ti3C2 (2.82 wt%) and Mo3C2 (2.29 wt%)). This comparison illustrates that the desorption performance of the different MXene systems can be affected by the choice of transition metal M and surface termination chemistry Tx, and that the desorption temperatures reported across the MXene literature can vary greatly from approximately 77 K to 371 K depending on the M-X-T system and the species being desorbed (Pal, 2024).

6. Comparative Analysis across Graphene, Borophene and MXene : The findings from the reviews in Sections 3-5 can be compiled to consider some cross-material trends. First, the pristine forms of all three 2D materials interact with H2 via weak van der Waals physisorption, in this case with baseline binding energies that span a relatively small range (0.03-0.14 eV per H2), none of which would be energetically practical for ambient-temperature reversible storage. Second, across the literature, the only strategies that are found to simultaneously shift the binding energy of H2 into the reversible 0.1–0.4 eV window and significantly boost the gravimetric storage capacity are decoration with light alkali metals (especially Li), or early transition metals (especially Sc, Ti, V, Zr), usually via electrostatic polarisation (alkali metals) and Kubas-type orbital hybridisation (TMs). Third, the peak gravimetric capacities of the borophene-based systems are the highest of the three families (up to 13.7 wt% for Li-decorated beta12 borophene), due to the low atomic mass of boron and its intrinsically electron-deficient, highly adsorptive lattice, which constitutes an additional storage channel not present in single-layer graphene or borophene (Alikhani, M., Hajibaba, 2024).

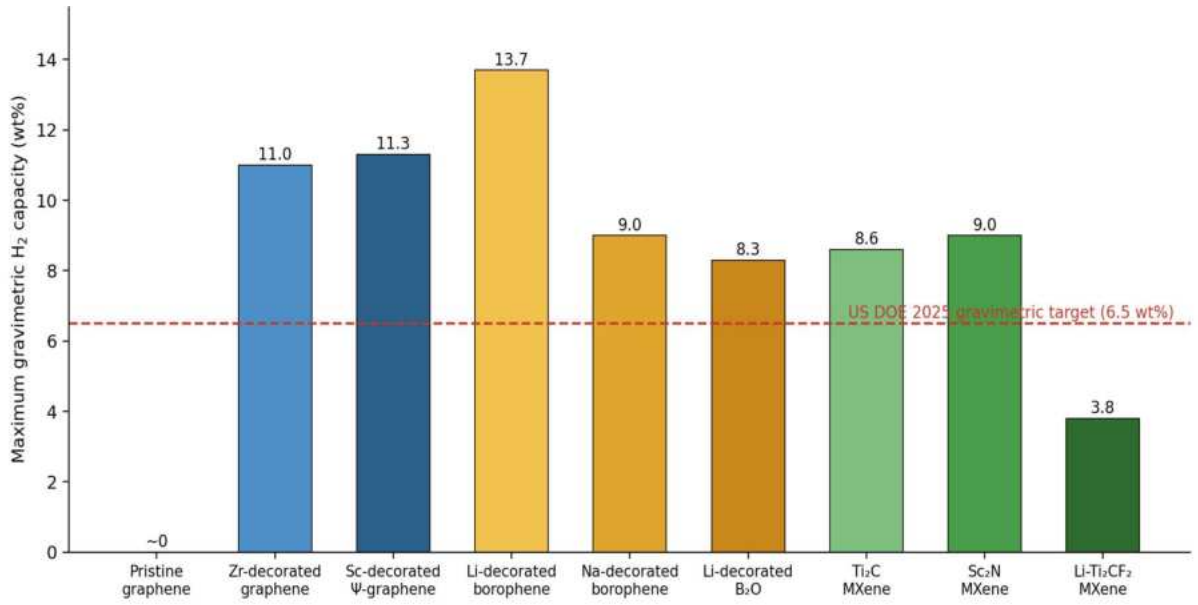

Figure 2. Comparison of DFT-predicted maximum gravimetric hydrogen storage capacities for representative pristine and metal-decorated graphene, borophene and MXene systems discussed in this review, benchmarked against the United States Department of Energy (DOE) 2025 ultimate gravimetric target of 6.5 wt%.

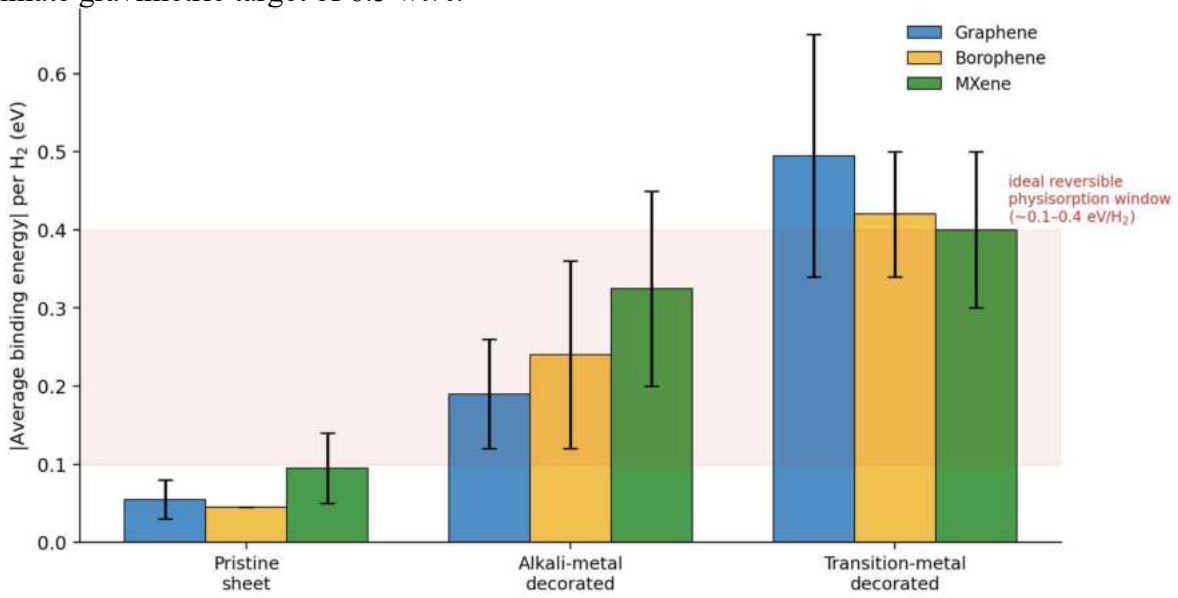

Figure 3. Average H2 binding energies obtained from DFT calculations on pristine, alkali-metal-decorated and transition-metal-decorated graphene, borophene and MXene surfaces, along with the corresponding range shown in the shaded band that typically marks the reversible storage window near ambient temperatures (0.1-0.4 eV per H2).

Table 2 provides a summary of the most representative system reported for each material family and key figures of merit derived from DFT calculations, and Table 3 compares the best-case values to the technical targets set by DOE for the practical performance of onboard hydrogen storage systems, which are the most commonly reported criteria in this area.

Table 2. Representative hydrogen storage systems with highest-performing graphene, borophene and MXene types, and the corresponding DFT figure of merits

Material Family	Best-Performing Reported System	Max. Gravimetric Capacity	Avg. Binding Energy (eV/H2)	Desorption Temp. (approx.)
Graphene	Sc-decorated Ψ-graphene	~11.3 wt%	-0.32 to -0.36	~400-410 K
Graphene	Zr-decorated graphene	~11.0 wt%	~-0.34	Not reported
Borophene	Li-decorated β12 borophene	~13.7 wt%	-0.12 to -0.36	Not reported
Borophene	Li-decorated honeycomb B_2O	8.3 wt%	-0.24	up to 500 K (stable)
MXene	Bare Sc_2N monolayer	~9.0 wt%	Kubas-type (chemisorbed H)	300 K (stable)
MXene	Multilayer $Ti_3C_2T_x$ (interlayer)	~3.8 wt% (theoretical max.)	N/A (confinement storage)	77-300 K studied

Table 3. Benchmarking of best-case DFT-predicted graphene, borophene and MXene hydrogen storage performance against the United States Department of Energy (DOE) technical targets for onboard light-duty-vehicle hydrogen storage systems.

Performance Metric	US DOE Ultimate Target	Best Graphene System	Best Borophene System	Best MXene System
Gravimetric capacity (wt%)	6.5	~11.3 (exceeds target)	~13.7 (exceeds target)	~9.0 (exceeds target, bare Sc2N)
System-level operating temperature	-40 to 60 °C	~130-140 °C equiv. (400-410 K)	Not consistently reported	Room-temperature stability reported
Reversibility (qualitative, from DFT)	Full, >1500 cycles	Generally favourable (physisorption/Kubas)	Generally favourable (physisorption)	Favourable for physisorbed H2; chemisorbed H less reversible
Primary technical risk	—	Metal-adatom clustering; ambient stability	Scalable single-phase synthesis; ambient oxidation	Termination-chemistry variability; interlayer control

The comparisons in these figures bring some positive expectations, but there are two cautions. First, the gravimetric capacities derived from DFT discussed in this review are material-level capacities for the idealised adsorbent only, whereas DOE targets are formulated at the system level, which includes the mass of the tank, valves and balance-of-plant. First, the gravimetric capacities derived from DFT discussed in this review are material-level capacities for the idealised adsorbent only, whereas DOE targets are formulated at the system level, which includes the mass of the tank, valves and balance of plant. Second, the highest reported

capacities in each material family are often linked to specific decorations or concentrations of defects or double-sided loading schemes that have not been realised in experiments at scale, and as such are not necessarily engineering targets (Arif, M., Li, Y., Zhang, 2025).

7. Challenges and Future Perspectives : Several scientific and practical issues arise repeatedly throughout the literature surveyed in this review and are directions for future work. The ability of decorated metal atoms to reduce surface energy by clustering into bulk-like clusters is the most commonly cited concern for all three types of materials, as it is difficult to create the well-dispersed, single-atom decoration assumed in most DFT models if the substrate is not carefully engineered (via vacancies, dopant sites, or curvature), and the loading density (in atoms per unit area) predicted by the calculations may not be achievable in experiments. A second recurring issue concerns ambient stability, especially for borophene, which has an electron-deficient boron lattice that is also predicted to have excellent storage properties but has been found experimentally to be rapidly degraded out of ultra-high vacuum and/or an inert atmosphere; strategies for encapsulating borophene are an active research area, and the deliberate use of more stable oxidised phases like borophene oxide is also being investigated to balance excellent predicted storage properties with practical handling requirements. Unlike the comparatively well-established large-area synthesis methods which are now available for graphene (chemical vapour deposition) and MXenes (selective wet-chemical etching of MAX phases), borophene has so far been grown as small-area films on specific metal substrates, namely silver and other metals, and not as a freestanding sheet, meaning that scalable, phase-pure synthesis of borophene remains a persistent hurdle.

The main challenges discussed in the reviewed studies are the difficulty in controlling the surface termination chemistry – except for one study, the Tx groups are largely determined by the etching chemistry and are not necessarily the specific terminations assumed in idealised DFT models – and the lack of knowledge of how to control interlayer spacing for the best performance: the nanopump-type confinement storage mechanism proposed in Section 5.3 is dependent on interlayer spacing, which remains unclear, and is not always achieved in the studies reviewed. Methodologically, the capacity for the subtle balance between physisorption and Kubas-type orbital interactions is still a subject of active benchmarking with different other higher-level methods, such as the random-phase-approximation or quantum Monte Carlo calculations, for smaller reference systems, and the fact that some multilayer Ti3C2Tx MXene studies show discrepancies between the gravimetric capacities predicted by DFT and those measured experimentally further emphasizes the need for close integration between computational screening and experimental testing. Finally, the accelerated search for the vast compositional space of doped, defect-engineered, and decorated 2D materials, achieved by staggeringly high-throughput DFT screening followed by machine learning surrogate models, is becoming a more and more popular strategy for discovering potentially viable hydrogen storage materials which could be more practically implemented through experimental synthesis and hydrogen-uptake measurement in the future.

8. Conclusion : In this review, the density functional theory (DFT) calculations of the hydrogen storage properties of three major classes of two-dimensional nanomaterials (2DNs), namely graphene, borophene and MXenes, have been compared. In all three, the binding energy and gravimetric storage capacity of the pristine sheets are enhanced significantly by weak physisorption of hydrogen, in several of the reported cases by far more than the DOE ultimate gravimetric target of 6.5 wt%, which is increased dramatically by decoration with light alkali metals or early transition metals, every time. Among the three families, lower atomic mass and

an electron-deficient lattice of the element boron offer higher peak capacities, while the compositional design space is unparalleled in the MXenes, and the Kubas-type interaction design and methodology has been transferred to both the newer families; graphene, the most studied and well-understood platform, offers the methodological and conceptual backbone. While significant hurdles lie ahead in achieving the full potential of these DFT predictions, the general picture painted by the literature reviewed in this work suggests that 2D nanomaterials, and metal-decorated 2D nanomaterials in particular, will continue to be among the most promising platforms for safe, lightweight and reversible solid-state hydrogen storage.

References :

1. Martins, N. F., Laranjeira, J. A., Azevedo, S. A., Fabris, G. S., Denis, P. A., & Sambrano, J. R. (2024). Two-dimensional materials applied to hydrogen storage. In Progress in Hydrogen Energy, Fuel Cells, Nano-Biotechnology and Advanced, Bioactive Compounds (pp. 83-115). Cham: Springer Nature Switzerland.
2. Mishra, R. K., Sarkar, J., Verma, K., Chianella, I., Goel, S., & Nezhad, H. Y. (2024). Borophene: A 2D wonder shaping the future of nanotechnology and materials science. Nano Materials Science, 7(2), 198-230.
3. Jayan, J. S., Raman, A., Deeraj, B. D. S., Sambasivam, S., & Saritha, A. (2026). Recent advances in borophene and its composites: perspective on its evolution, properties, and future applications. Critical Reviews in Solid State and Materials Sciences, 1-46.
4. Ajmal, S., Huang, J., Singh, M., Kumar, A., Guo, J., Tabish, M., ... & Yasin, G. (2025). Realizing electrochemical energy conversion and storage with borophene: science, engineering, obstacles, and future opportunities. Small, 21(10), 2411311.
5. Bilgiç, G. (2024). Review of properties, synthesis, and energy applications of borophene, a novel boron-based 2D material. Journal of Boron, 9(2), 82-95.
6. Ghotia, S., Kumar, P., & Srivastava, A. K. (2025). A review on 2D materials: unveiling next-generation hydrogen storage solutions, advancements and prospects. Journal of Materials Science, 60(3), 1071-1097.
7. Yadav, S., Sadique, M. A., Kaushik, A., Ranjan, P., Khan, R., & Srivastava, A. K. (2022). Borophene as an emerging 2D flatland for biomedical applications: current challenges and future prospects. Journal of Materials Chemistry B, 10(8), 1146-1175.
8. Wang, G., Zhang, H., Zuo, H., Wang, H., Beshiwork, B. A., Teketel, B. S., ... & Lin, B. (2025). Ensemble learning enables accurate and interpretable identification of hydrogen storage in 2D materials beyond MXenes. Renewable Energy, 124229.
9. Gupta, S., Mayilswamy, N., Kandasubramanian, B., Kumar, A., Emadian, S. S., & Krishnamurthy, S. (2025). Exploring borophene: pioneering trends in energy storage materials. Journal of Nanoparticle Research, 27(3), 71.
10. Joseph, J., Sivasankarapillai, V. S., Nikazar, S., Shanawaz, M. S., Rahdar, A., Lin, H., & Kyzas, G. Z. (2020). Borophene and boron fullerene materials in hydrogen storage: opportunities and challenges. ChemSusChem, 13(15), 3754-3765.
11. Bakhit, M. A. S. (2023). Theoretical Investigation on Hydrogen Storage Performance of MXENE Mo2C. University of Johannesburg (South Africa).
12. Liu, Z., Zhao, W., & Chai, M. (2024). Li-decorated bilayer borophene as a potential hydrogen storage material: A DFT study. International Journal of Hydrogen Energy, 51, 229-235.

13. Macilon, P. G., Santos, T. F., Santos, E. V., Carvalho, B. R., & Nascimento, J. H. O. (2025). Advances in 21st century on borophene-based nanomaterials for next-generation energy technologies. Emergent Materials, 8(6), 3893-3934.
14. Ibrahim, M. A., Mahmoud, A. H., Soliman, K. A., Mekhemer, G. A., Ahmed, M. N., Shawky, A. M., ... & Moussa, N. A. (2022). Borophene and pristine graphene 2D sheets as potential surfaces for the adsorption of electron-rich and electron-deficient π-systems: a comparative DFT study. Nanomaterials, 12(6), 1028.
15. Pal, P., & Nandi, M. (2024). Recent advances in the syntheses and emerging applications of 2D borophene-based nanomaterials with a focus on supercapacitors. Dalton Transactions, 54(1), 38-58.
16. Alikhani, M., Hajibaba, S., Moayedi, M., & Abdi, Y. (2024). Borophene–MXene heterostructures as supercapacitor. Journal of Energy Storage, 99, 113301.
17. Makaremi, M., Mortazavi, B., & Singh, C. V. (2018). 2D Hydrogenated graphene-like borophene as a high capacity anode material for improved Li/Na ion batteries: A first principles study. Materials today energy, 8, 22-28.
18. Arif, M., Li, Y., Zhang, Q., Tang, Y., & Wang, H. (2025). Computational Design of 2D Materials for Zinc-Ion Batteries Using Density Functional Theory Calculations. Advanced Theory and Simulations, 8(11), e01346.
19. Martins, N. F., Laranjeira, J. A., Lima, K. A., Ribeiro, L. A., & Sambrano, J. R. (2026). DFT Investigation of Two-Dimensional Borospherene for Sensing and Capture of Toxic Gases. ACS Applied Nano Materials, 9(11), 5045-5053.
20. Hussein, U. A. R., Hammad, A. K., Saydaxmetova, S., Yaseen, B. M., Albadr, R. J., Taher, W. M., ... & Islam, S. (2025). A DFT study for evaluation of the electrochemical performance of hydrogen boride monolayer as anode for Mg-ion battery. Journal of Energy Storage, 133, 118084.
21. Sura, A., Narwal, S., Singh, A., Singh, A., Sehrawat, V., Dahiya, B., ... & Nain, S. (2025). Unveiling the Versatility of Borophene for Sustainable Technological Innovations: A Review. Energy & Fuels, 39(49), 22998-23028.
22. Haldar, S., Mukherjee, S., & Singh, C. V. (2018). Hydrogen storage in Li, Na and Ca decorated and defective borophene: a first principles study. RSC advances, 8(37), 20748.

•