Carbon Nanomaterials as One of the Options for Hydrogen Storage

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Abstract For the Hydrogen economy, cost-effective and safe storage of hydrogen assumes importance. Among the various modes of storage, solid-state storage has definite advantages for mobile and stationary applications. However, among the probable solid-state materials, the desired levels of storage (~6 Weight %) can be possible in carbon materials suitably modified with activation centers. A variety of modifications of carbon materials have been examined for hydrogen storage. However, the search has to continue till the desired levels of storage under ambient conditions are achieved.

Keywords Hydrogen storage · Carbon nanomaterials · Graphene · Activation centers · Carbon allotropes · Solid-state storage

1 Introduction

The energy needs of the world have been centered around carbon-based materials for a number of centuries. There are various forms of carbon materials that are available. It appears that the variety of carbon forms may be endless, and a simple classification is given in Table 1.

Five decades ago, a concept based on the Hydrogen Economy has been evolving and the transformation towards this economy essentially depends on the three components namely generation, storage, and delivery of hydrogen. There are consistent attempts to generate hydrogen from the decomposition of water (from renewable sources) and this pursuit is an ongoing exercise to make this process economically feasible, though the desired level of success is still to be achieved. Commonly available methods for the storage of hydrogen, namely in high-pressure gas cylinders (up to 800 bar) and as liquid hydrogen in cryogenic tanks (at 21 K) are energy inefficient and not safe for certain applications, especially for mobile applications. Hydrogen

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Table 1 A classification scheme for carbon allotropes, molecular crystals, and derived forms

Sp^3	Sp^2	Sp^1
Diamond Cubic Hexagonal	Graphite Hexagonal Rhombohedral	Carbyne A-Carbyne B-Carbyne Chaoite
$Sp^3 + Sp^2 + Sp^1$	Sp^n ($3 < n > 1, n \neq 2$)	
Mixed forms of carbon	Intermediate forms of carbon	Intermediate forms of carbon
Amorphous carbon Glassy carbon Carbon black Adamantine carbon	$3 > n > 2$ Fullerene C_X $X = 60, 70, 84$ (When $x = \infty, n = 2$) Carbon onions Carbon nanotubes	$2 > n > 1$ Cyclo (N) carbons $N = 18, 24,30$ (When $N = \infty, n = 1$)

adsorption/absorption on solid materials with high specific surface area and chemically bonded in covalent and ionic bonds appears to be attractive. Materials such as metal hydrides, alloys, complex hydrides, and high surface area porous materials are showing an affinity for ab(ad)sorbing large amounts of hydrogen. However, each of these storage materials suffers from some particular drawbacks. These materials crystalize in closed packed configurations giving rise to tetra-/octahedral- or other voids thus possibly restricting one hydrogen species per void space at room temperature and atmospheric pressure, which means the weight percent of storage capacity depends on the atomic or molecular weight of the nature of solid storage medium. In the solid-state hydrogen storage, hydrogen is bonded by either physical forces (Physical adsorption or van der Waals forces), e.g., MOF and carbon-based materials, or chemical forces (chemisorption involving chemical bonds), e.g., hydrides, imides, and nitrides. Physisorption has the advantages of higher energy efficiency and faster adsorption/desorption cycles, whereas chemisorption results in the adsorption of larger amounts of gas but in some cases, is not reversible and requires higher temperatures to release the adsorbed gas which is not suitable for mobile applications.

The development of hydrogen storage materials with lightweight, high capacity, high stability, and better safety is imperative for portable electronics and transport applications. Carbon-based materials with different (allotropic) forms and chemical affinity are favorable for hydrogen storage application due to their low atomic weight, high surface area, porous nature, and higher safety characteristics. Carbon can be hybridized in Sp, Sp^2, and Sp^3 bonds, and exist in 0D, 1D, 2D, and 3D forms. Additionally, chemical and physical properties of these materials can be altered by using its different sources, composites, functional derivatives, or doping with other elements. It may possess pores of different shapes and sizes, which are ideal physisorption/ ad(ab)sorption sites for hydrogen storage. In the following, the hydrogen storage capacities of different carbon nanostructures, including activated carbon, graphite, graphene, CNTs, fullerene, and CNFs, are discussed. The attempts to store on modified (especially metal loaded) carbon materials also will be considered. Recent and relevant efforts for improving the hydrogen storage capacities are also considered. There are a variety of these materials and nature has shown that this is one of the potential storage media for hydrogen (in the form of hydrocarbons) and also shown that storage can go up to 25 weight percent (as in methane). However, one must be aware these hydrocarbon molecules are covalent in nature and thus may not readily release hydrogen when required as in transport applications. In this presentation, the scope of carbon materials for hydrogen storage application is considered.

The microporosity of carbon materials is not directly related to hydrogen storage application but a nearly linear relationship has been realized with respect to BET surface area, typical plots can be seen in the following reference and references cited therein [1]. There have been many attempts to modify the surface of carbon materials so that the storage capacity can be increased. One such attempt deals with the presence of heteroatoms on the surface of carbon materials for various reasons like the possibility of dissociating molecular hydrogen or facilitating the spill-over process However, the current situation with respect to hydrogen storage in carbon materials with heteroatoms can be stated that typically N-doping is only apparent when considering the hydrogen uptake as a function of microporosity (rather than total porosity). This possibly leads to the conclusion that pores larger than the micropore size range have a lesser role in hydrogen storage capacity.

The advanced design and testing of carbon materials for energy storage devices appear to be important. The main shortcomings of these materials are related to irreversible capacity loss, big voltage crosstalk, and low density [2]. Novel composites containing multifunctional nanostructured carbon and other dopants can synergistically take advantage of the combination of ordered building block units with other desired properties. Since most physisorption is involved in this process of hydrogen storage, only a small amount of hydrogen could be stored even at a pressure of 90 bar. Obviously, temperature (~room temperature) will have an almost negligible effect on hydrogen storage capacity.

2 Activated Carbon

Activated carbon is one of the widespread and commercially used porous carbon materials, consisting of graphite crystallites and amorphous carbon. It has been used for centuries as an adsorbent due to its good adsorption capacity, high specific surface area (up to ~3000 m^2/g), porous structure, inertness, surface reactivity, and thermal stability. The pores range from micro to macro size with an abundance of micro-sized pores of <1 nm. Due to its widespread pores, it is a potential material for hydrogen storage. In general, the hydrogen adsorption on such materials is proportional to the specific surface area (SSA) and pore volume. Several research efforts are devoted to finding the hydrogen uptake in activated carbon materials with different pore sizes, pore volume, and specific surface area. Most of the experimental findings have demonstrated the hydrogen storage capacity of activated carbon as 2.5 and 5.5 wt.% at low pressure (1–10 bar) and high pressure (up to 60 bar), respectively. It was observed that at 100 bar and room temperature, the hydrogen uptake of activated carbon was <1 wt.%, even with a highly porous structure and high specific surface area. It has been observed by different researchers that the optimum pore size in activated carbon for hydrogen storage is 0.6 nm. Table 2 shows the experimental results reported (complied) of hydrogen storage capacity of activated carbons at different temperatures and pressure conditions. Different chemical treatments and doping of activated carbon were also utilized to improve the hydrogen uptake of activated carbon materials. However, they do not meet the U.S. Department of Energy (DOE) target, and further efforts are needed to realize their potential for enhanced hydrogen storage capacity.

One can assess that the highest value of excess adsorption of hydrogen reported for a commercial activated carbon is around 5 wt.% at 77 K and pressures from 3 to 6 MPa. In the case of activated carbons prepared on a laboratory scale, the best value obtained is ~7 wt.% at 77 K and 20 MPa. Most of the studies reported in the literature mainly concentrated on increasing the surface area of the activated carbon (by an appropriate method for (mostly chemical) activation) and the porosity of the material. The linear correlations connecting adsorption capacity and physical parameters like surface area and pore volume of activated carbons have been attempted but the results available indicate only limited applicability. It is also to be noted that activated carbons show hydrogen adsorption capacities at cryogenic conditions and this is not very suitable for the applications envisaged for hydrogen economy.

Table 2 Data on hydrogen storage capacities of different activated carbon materials (Data from literature)

Adsorbent employed	Reported hydrogen storage (wt.%)	Conditions (temperature and pressure)
Activated carbon	0.67	303 K 10 MPa
Activated carbon	1.4	77 K 0.1 MPa
Activated carbon	1.6	298 K 13 MPa
Activated carbon	4.5	77 K
Activated carbon	5.7	77 K 3 MPa
Activated carbon	3.2	298 K 20 MPa
Activated carbon	6/5	298 K 50 MPa
Chemically activated carbon	8.0	77 K 4 MPa
Activated carbon	2.3–5.8	77 K 4 MPa
Activated carbon (treated with KOH)	6.6	4 MPa
Activated carbon (activated with Ni)	1.8	77 K 0.1 MPa
Activated carbon (activated with Pt)	2.3	298 K 10 MPa
Activated carbon (activated with Pd)	5.5	298 K 8 MPa

3 Graphite

Graphite has Sp^2 hybridized carbon atoms arranged in a hexagonal lattice with a layered structure such that the layers themselves are held together by van der Waals forces of interaction. Graphite can be naturally obtained or can be artificially prepared. It is also widely explored for hydrogen storage applications. Various studies have modified their porosity, chemical bonding, and surface area by using different activation methods as well as doping them with different metals. Ball-milled graphite and intercalated graphite are widely explored for hydrogen storage applications. Ball-milled graphite contains tremendous defect sites and high surface area, which lead to chemisorption resulting in high hydrogen storage capacity. The ball-milling-induced rupture of graphite sheets and the emerging active edges and defects on the fragmented part are also confirmed by neutron scattering and spin resonance studies.

4 Graphene: The Hydrogen Adsorption/Desorption Isotherm

The hydrogen adsorption/desorption isotherm of the nitrogen-doped graphene, Graphitic Oxide and Graphite powder is shown in Ref. [3]. The hydrogen adsorption isotherm has been carried out at 298 K and 90 bar pressure. The nitrogen-doped graphene material showed nearly ~1.5 wt.% hydrogen storage capacity at room temperature and 90 bar pressure. In this context, the graphitic oxide (GO) showed ~0.21 wt.% hydrogen storage capacity at room temperature and 90 bar. This value is less than that of nitrogen-doped graphene material. However, nitrogen doping of graphene materials takes up substitution positions in the carbon lattice, there is transportation of hydrogen atoms on to the graphene surface. Furthermore, these results reveal that the nitrogen doping on graphene materials can extensively modify the catalytic effect of the graphene materials for hydrogen dissociative adsorption, foremost for the improvement of the dissociative hydrogen adsorption. This observation suggests that the nitrogen atoms possibly take part in a role in the hydrogen adsorption capacity at room temperature. A previous study recommended that the presence of nitrogen atoms in graphene sheets increases the enthalpy of hydrogen adsorption [4]. Potentially almost all the adsorbed amount can be desorbed which is an interesting characteristic expected for hydrogen storage materials. Various attempts have been made to modify or adopt different preparation procedures for graphene materials and it has been shown that N and P doping in graphene does not improve the materials' hydrogen storage capacity [5]. It has been proposed that the hydrogen binding energy can be tuned as a function of the graphene local curvature. The adsorption is facilitated by convex sites and desorption is facilitated on concave sites. The corrugation of graphene flakes and its control with large variety of functionalization may make these materials can impact in the search for hydrogen storage [6].

5 Modification of Activated Carbon

For conventional activated carbon materials, the hydrogen uptake is proportional to the surface area and pore volume; and normally the data are fitted well with the Langmuir isotherm model (monolayer adsorption). High adsorption capacity is only obtained at extremely low cryogenic temperatures and high pressures. Hydrogen adsorption on various types of commercial and modified activated carbon products has been extensively studied. Experimental results show that products with micropore volumes greater than 1 mL/g are able to store ca. 2.2 wt.% of hydrogen due to physisorption and it is expected that optimization of the adsorbent and sorption conditions could lead to a storage capacity of 4.5–5.3 wt.%. Agricultural waste materials such as coconut shells, coconut fibers, jute fibers, nut shells, oil seeds, etc., are popular raw materials for producing activated carbon materials. Carbon materials and their activation have been extensively discussed in Ref. [7]. Jin et al. [8] prepared activated carbons with different porosities using chemically activated coconut shells. They reported a maximum hydrogen adsorption capacity of 0.85 wt.% at 100 bar and 298 K. Sharon et al. [9], produced activated carbon fibers (ACF) using soybean and bagasse. The authors measured hydrogen storage capacities of 1.09–2.05 wt.% at a pressure of 11 Pa and room temperature. Another form of AC, the advanced AC monoliths, with good mechanical strength (maximum compression strength of 22 MPa), high volume of micropores (up to 1.04 cm^3/g), and high density (up to 0.7 g/cm^3) have been shown to adsorb 29.7 g/L of hydrogen at 77 K and 4 MPa [9]. Mechanically milled AC consists of some form of defective nanostructure, which increases the specific surface area. Research findings have revealed that after 10 h of milling, the hydrogen storage capacity increases from 0.90 wt.% to ca. 1.7 wt.%. Studies have shown that the loading of precious metals, e.g., Pt, onto AC, increases the adsorption capacity. The merging of the two adsorption phenomena, i.e. chemisorption (on the Pt surface) and physisorption (on the carbon surface) gives rise to a significant amount of spillover hydrogen.

6 Carbon Nanotubes

Ever since the discovery of carbon nanotubes was reported in 1991, there have been various attempts to use this new type of carbon material for hydrogen storage. These studies have led to some unexpected levels of storage up to nearly 60 wt.% or even more. However, the consensus now is that these reports claiming over 60 wt.% are flawed by experimental aberrations.

Only limited data are given in Table 3. For more extensive compilations, one is directed to references [35]. Various nanotubes like carbon nanotubes, boron nitride nanotubes, silicon carbide nanotubes, carbon nano-scrolls, pillared Graphene, and porous nanotube network materials have been extensively investigated and the final suggestion is that one should design novel materials with the following key parameters namely high accessible surface area, large free pore volume and strong interactions between the surface-active sites and the substrate hydrogen.

In a recent review, Lyu et al. [36] propose that “a detailed study of the optimum number of metal atoms without aggregation on CNT should be performed. (1) At the same time suitable preparation methods for realizing controllable doping sites and doped configurations should be devised; (2) The material synthesis, purification, and activation methods have to be optimized; (3) Active sites, molecular configurations, effectively accessible surface area, pore size, surface topology, the chemical composition of the surface, applied pressure and temperature, defects, and dopant,

Table 3 Selected data (for comparison) on the storage of hydrogen by carbon nanotubes

Sample	Temp (K)	P (MPa)	Hydrogen storage (wt.%)	Refs.
Herring bone GNFs	RT	11–35	67.5	[10]
Platelet GNFs	RT	11–35	53.68	[10]
Graphitic nano fibers	RT	101	10	[11]
Graphitic nano fibers	RT	8–120	10	[12]
SWNTs (low purity)	273	0.4	5–10	[13]
SWNTs (high purity)	80	70–80	8.25	[14]
SWNT (high purity + Ti alloy)	300–600	0.7	3.5–4.5	[15]
Li-MWNTs	473–673	1	20	[16]
Li-MWNTs (K0MWNTs)	473–673	1	2.5 (1.8)	[17]
MWNTs	RT	Ele-	<1	[18]
SWNTs	300–520	1–100	0.1	[19]
Various CN	RT	1	<0.1	[20]
SWNTs (+ Ti alloy)	RT	35	0	[21]
SWCNT	RT	0/8	4.5	[22]
SWCNT	295	10	0.93	[23]
SWCNT	RT	0.1	1.2	[24]
SWCNT	323	4.8	4.77	[25]
SWCNT	–	–	−0.8	[26]
MWCNT	–	3	2	[27]
MWCNT	77	0.005	0.54	[28]
MWCNT	298	0.1	0.2	[29]
NWCNT	425	10	3.8	[30]
MWCNT	143	3	3.5	[31]
MWCNT	RT	7.5	1.5–2.1	[32]
MWCNT	–	–	2.7–3.8	[31]
Carbon nano onion	77	1.5	>18.2	[33]
g-C_3N_4 nanotubes	RT	37	0.78	[34]

which are some of the important factors that strongly affect the hydrogen absorption in carbon nanotubes" should be elucidated.

In contrast, Lobo et al. [37], propose carbon nanostructures are promising materials for hydrogen storage applications. They emphasize that hydrogen can be physisorbed in carbon nanotube bundles on various sites such as external wall surfaces, grooves, and interstitial channels. Therefore, it can have a large energy density (as required for mobile applications). It is also known that by tuning the adsorption conditions, hydrogen can be either chemisorbed or physisorbed in carbon nanotubes. In a review, Lee et al. [38] and others [39] propose that a more detailed understanding of the interfacial interactions between adsorbent and adsorbate should be evolved and the phenomenon of spill-over can contribute to adsorbent surfaces to achieve the desired levels of hydrogen storage.

7 Impact of Structures on Hydrogen Storage in Different Carbon Materials

Increasing hydrogen storage to the levels advocated by DOE through materials in the nanoscale has been proposed and intensively researched but the success appears to elude us. Among the several options available, various allotropic forms of carbon, like CNTs, graphene, and activated carbons have been considered to be appropriate systems owing to their unique properties like high surface area, (this parameter has limited linear variation with absorbed hydrogen) porous nature (but pore volume is limited for each material) and high thermal and mechanical stability, and all these have been so far considered though questionable, as vital factors for hydrogen storage. Emphasis has been given to the hollow and porous structure of CNTs which is supposed to give the possibility of hydrogen storage both in the inner and outer surfaces that are well investigated by many theoretical as well as experimental studies. These studies though have relevance did not answer the stumbling block in achieving the goal of reaching the DOE standards. CNTs are termed to be one of the promising nanostructures for hydrogen storage however this expectation also has not yielded the desired result.

Moreover, the simultaneous presence of defects, both topological and structural types, and other irregularities affect the activation and adsorption and hence the amount of hydrogen stored in the system. In addition to this, doping also leads to structural and electronic property variations. However, these modifications so far have not shown enormous improvement in hydrogen storage capacity. It is however believed that estimated values of hydrogen storage still show the high impact of structure on the storage capacity. Nanomaterials are also analyzed and found that some of these strongly affect the storage capacity. But still, the DOE target could not be achieved which makes this issue an interesting topic of study even today.

Different types of nanotubes like metallic and semiconductor (also single or multi-walled) with varying structures were considered. It has been observed that the adsorption binding energy values as a function of different orientations of adsorbed species and at different sites of nanostructures are compared and the results show the strong impact of CNT structure on the storage capacity of hydrogen. Hydrogen can be adsorbed on graphene in two different ways: physisorption or chemisorption. While the first one is due to Van Der Waals interaction, the second is by forming a chemical bond with the C atoms. Physisorption usually happens with hydrogen in molecular form and in chemisorption, dissociation of H_2 into atomic hydrogen takes place and is a rather favorable process unlike in CNTs where physisorption is the most preferred way of storage. A single graphene layer is a quasi-2D system, and its VD is not well defined, thus in the evaluation of the potentialities of graphene for hydrogen storage, different forms of graphene such as multilayers, three-dimensional assemblies, or nanostructures of graphene are considered. However, it should be remarked that the standards for the necessary hydrogen storage for the projected applications should be realized at the earliest.

8 Modified Carbon Materials for Hydrogen Storage

Modification of the equipotential surface of carbon materials has been attempted for various reasons. Usually, the activation is aimed at introducing active centers on supported phases. It is usually to disperse active metals so that the exposed metal surface area is maximum. Hydrogen adsorption involves dissociation of molecular hydrogen and any storage medium should have dissociating centers for molecular hydrogen. Recognizing this aspect, heteroatom substitution has been proposed as one of the options. DFT calculations have also shown that molecular hydrogen dissociation energy is considerably reduced on heteroatoms like N, P, or B substituted carbon surfaces (Table 5), however, these studies so far have not led to the levels of storage of hydrogen on these materials.

8.1 Nitrogen Doping in Carbon Materials

Nitrogen is an abundant (80%) element in the terrestrial atmosphere. Molecular nitrogen is stable and has a minor role in the lower atmosphere. N-doped carbon materials are the much-studied area in energy storage. Depending on the type of N bonding within the carbon matrix, nitrogen can share one to two π-electrons with the π-electron system of the carbons. This sharing of electrons causes an *n*-type doping if N atoms directly substitute the C atoms in the graphitic lattice. N-doping in carbon generally manifests itself in three different forms namely, pyrrolic-N, pyridinic-N, and quaternary-N, and each form alters the carbon electronic band gap differently. The band gaps of pyrrolic-N, pyridinic-N, and quaternary-N-doped carbons are reported to be 1.20, 1.40, and 1.39 eV, respectively.

Particularly, all materials obtained by these techniques have a nitrogen content lower than 10 atoms % because of the high temperature environment that was used in carbonization. An alternate synthesis method needs to be developed that enables the preparation of carbon material with high nitrogen content and time they should be stable at high temperatures. It will be beneficial if one can adopt a polymerization and low-temperature growth process to create nitrogen-doped carbon materials.

Nitrogen is essentially introduced into the carbon matrix in two ways, either by the carbonization of N-containing precursors or by post-modification methods. The common nitrogen-containing precursors are urea, melamine, cyanide, polyacrylonitrile, and ammonia. Another resourceful approach for the synthesis of N-doped carbon materials is based on naturally (sustainable) nitrogen-containing precursors

Table 4 Bond length and dissociation energy of hydrogen on the CNTs calculated using B3LYP with 6.31G (P,D) basis set on the UFF optimized structures [40]

Substitution	Total energy (Hartrees)	Bond length H_1–H_2 (Å)	Dissociation energy (eV)
Hydrogen	−1.175	0.708	4.76
CNT CNT + H_2	−3686.5502 −3687.7161	…… 0.776	… 4/51
NCNT NCNT + H_2	−3702.5908 −3703.5989	… 0.815	…. 0.22
PCNT PCNT + H_2	−3989.1694 −3990.2550	…. 0/815	… 2.33
SCNT SCNT + H_2	−4046.0020 −3047.0067	… 0.817	…. 0.13
BCNT BCNT + H_2	−3671.7254 −3672.9440	…. 0.818	…… 5.95
2BCNT (adjacent) 2BCNT (adjacent) + H_2	−3658.6666 −3659.8092	…. 0.813	… 3.88
2BCNT (Alternate) 2BCNT (alternate) + H_2	−3659.3491 −3660.3594	…… 0.928	…… 0.28

Table 5 Technical system targets for on-board hydrogen storage for light-duty fuel cell vehicles

	2020	2025	Ultimate
Usable specific energy from H_2 [kWh/kg]	1.5	1.8	2.2
Net usable energy/mass system mass [kg H_2/kg system]	0.045	0.055	0.065
Usable energy density from H_2 [kWh/L]	1.0	1.3	1.7
Net usable energy/max system volume [kgH_2/L system]	0.030	0.040	0.050
System cost [USD/kWh net]	10	9	8

like amino-carbohydrates or other N-enriched polymers, amino acids, proteins, N-ionic liquids, and waste crab shells. Another possible way is to pyrolyze the nitrogen and carbon-containing precursors, such as heterocycles or melamine, by which direct incorporation of nitrogen atoms into the forming of carbon backbone becomes possible. One of the procedures for deriving N-doped carbon is hydrothermal treatment of carbohydrate-rich biomass. Using nitrogen-containing biomass-related precursors and hydrothermally treating them yields nitrogen-containing carbonaceous materials that offer tremendous possibilities for further treatments and energy applications. The application of nitrogen-doped carbon materials has been investigated as a material for hydrogen storage at room temperature and ambient pressure [41]. It has been reported that nitrogen-enriched graphitic carbon material exhibits a hydrogen storage capacity of 0.34 wt.% at 298 K under 100 bars [42]. It has also been reported that the addition of N-species in mesoporous carbons showed hydrogen adsorption capacity of 1.1 wt.% at 298 K and 100 bar pressure [43]. It has also been reported that the microwave plasma CVD process enables the growth of specific nanostructured nitrogen-doped carbons. Nitrogen incorporation into these forms of carbon is approximately 1 at.%. It shows a gravimetric hydrogen storage capacity of 0.7–0.8 wt.% under 300 K and 0.1–7 MPa [44]. Hydrogen adsorption on nitrogen-doped carbon xerogels showed maximum hydrogen uptake of 0.28 wt.% at 308 K [45].

8.2 Phosphorus-Doping in Carbon Materials

The changes in the physical properties of Sp^2 carbon motifs after the addition of phosphorous into their lattice are considered. However, P has a larger atomic radius and higher electron-donating ability, which makes it an option as a dopant. Phosphorus is not a common element in carbons, although it is present in carbons obtained using phosphoric acid activation. Due to the addition of P in the carbon matrix, the density of states near the Fermi level is also found to increase, which increases with the increase in the P-doping level. In these reactions, the formation of phosphate and polyphosphate bridges provokes the expansion and cross-linking of the carbon matrix, driving to an accessible pore structure after the removal of the acid. The chemical state of phosphorus in carbons is a rather controversial issue. Some experimental evidence using different analytical techniques (FTIR and XPS) has shown that the most abundant P species introduced in carbons by phosphoric acid activation are –C–P– or –C–O–P bonds in phosphate and phosphonate-like structures. The XPS analysis further allowed for an insight into the binding states, proving the true incorporation of the phosphorus atoms into the graphite sheets, besides some P–O binding sites, most likely on the surface of the material. The existence of pentavalent phosphorus and elemental phosphorus is very infrequently detected, except when high temperatures are applied. Recent studies have reported that P-containing groups might be significant for the progress of graphitic crystallites which contrasts with far reported role of P as an inhibitor of carbon graphitization. Yang et al. [46] reported that phosphorous-doped ordered mesoporous carbon was synthesized by co-pyrolyzing a phosphorus-containing source and a carbon source collectively using ordered mesoporous silica (SBA-15) as a template without the use of any metal components. More recent approaches have recognized dissimilar synthetic pathways in the direction of phosphorus-doped carbon materials, proving themselves as promising candidates for energy storage applications. It has been shown in the previous section that carbon materials with substitution by heteroatoms like N, S, and B, show hydrogen sorption capacity. However, the effect of substitution of phosphorus in carbon materials has not been investigated to the same extent.

8.3 Boron-Doping in Carbon Materials

Boron is an element with unique properties. It is thus an interesting candidate for doping of carbon materials, modifying the properties of pure carbons. Several researchers have started focusing not only on basic studies on B-doping, but also on applying the obtained materials and exploiting their favorable properties in energy-related applications. Due to its three valence electrons, B is well thought-out as a good dopant. Substitutional boron enhances the graphitization of carbon. It has been found that boron atoms are favored to be substituted in the graphite lattice. The existence of B–C bonds in the carbon framework can lower the Fermi level of the structure and then tune the properties of oxygen chemisorption and electrochemical redox reactions. The synthetic procedure, in which elemental B and graphite powder served as precursors, yielded a mixture of different B-containing carbon nanostructures, such as thin graphitic sheets, tubes, and filaments. The substitutional doping of carbon atoms in Sp^2 and Sp^3 configurations with boron can modify the electronic and structural properties of the resulting carbon. Over the years boron-doped carbons have been synthesized by standard CVD process using BCl_3. Substituted boron atoms in the carbon lattice accelerate the graphitization and suppress the oxidation of carbon materials, which seems promising for their use as reinforcement materials in aerospace applications. The positive effect of boron doping on diamond and carbon electrodes and in the field of hydrogen storage has also been reported, although further optimization of the boron doping environment seems yet to be needed.

The storage of hydrogen in carbon nanomaterials requires appropriate chemical activators in suitable geometry. Sankaran et al. reported different types of carbon materials employed for the hydrogen sorption capacity. The storage capacity of 2 wt.% at 298 K and 80 bar pressure is obtained for boron boron-substituted carbon nanotube. However, a maximum storage capacity of 2 wt.% is attained at 80 bar and 300 K for boron-containing carbon nanotubes (BCNT) whereas pure carbon nanotubes (CNT) show only 0.6 wt.% at 300 K and 80 bar and B-doped bulk carbon material (PBC) shows only 0.2 wt.%. Mike Chung et al., reported the microporous boron-substituted carbon (B/C) materials show a significantly higher hydrogen binding energy and reversible hydrogen physisorption capacity of 0.6 and 3.2 wt.%

at 293 and 77 K, under 40 bar of hydrogen pressure [47]. B-containing polymeric precursors and pyrolysis were employed to synthesize microporous B/C materials with a high B content (7.2%) and high surface area (780 m^2/g). The substitutional B elements in B/C material serve as internal p-type dopants and polarize the C surface, which exhibits a significantly higher hydrogen binding energy [48]. For efficient hydrogenation and hydrogen storage, these boron atoms should be incorporated geometrically and chemically into the carbon network. Wang et al. reported that B- and N-doped microporous carbon had a hydrogen storage capacity of 0.55 wt.% at 298 K and 10 MPa. By doping 6.0 wt.% Ru metal on the B- and N-doped microporous carbon, the hydrogen uptake at 10 MPa was increased to 1.2 wt.%, i.e. The improvement of hydrogen storage was due to the spillover of atomic hydrogen from the Ru metal particles to the B-and N-doped microporous carbon [49].

9 Perspectives

The standards that one wishes to achieve in the storage of hydrogen are:

- Gravimetric H density in the range of 5–10 wt.% H_2, and energy density of 1.6–3.2 kWh/kg.
- Volumetric H density >50 kg H_2 m^{-3} and energy density >1.6kWh/L.
- Thermodynamics: T 0 < 85 °C (transport applications) or <200 °C (stationary applications).
- Kinetics (tank level): fill time 3–5 min; H_2 release flow 1.6 g/s.
- Durability: 1500 cycles (1/4 tank to full).

One of the recent specifications and the time to achieve them are assembled in Table 5.

Of all the available hydrogen storage materials, why carbon materials are preferred option? What is the maximum hydrogen storage capacity that can be expected and what will be the limit that can be practically achieved? It may be remembered that nature mostly provides hydrogen source in combined form with carbon and oxygen though other elemental compositions are also possible. If carbon materials can be obtained in an atomic state, then the maximum storage capacity can be expected to be around 25 wt.%. However, since it is not possible to get atomic hydrogen, the carbon materials can be obtained at the limit with one vacant valency in carbon two-dimensional material and the maximum storage can be expected to be 6.25 wt.%. This limit is arrived at assuming that hydrogen is held by the solid by valence forces. If hydrogen is stored or retained by other forces, this limit may not hold good.

If the stored hydrogen were to occupy the interstitial sites in carbon materials, then the energetics of storing and releasing should also be considered for practical application.

Since normally carbon materials are microporous in nature, hydrogen may be held in these pores by condensation forces and hence one can hope for higher storage capacity, however, the experimental variables for this process namely temperature and pressure have to be different from normal ambient conditions.

10 Conclusion

Hydrogen storage characteristics and treatments for improving the storage capacities of different carbon materials are presented. The following deductions can be stated:

1. The hydrogen storage capacity of carbon materials depends upon surface area, which is affected by micropore size distribution that counts for the presence of narrow micropores.
2. Thermal treatments and metal doping on carbon nanostructures are observed to be useful for improving hydrogen storage capacities but higher storage capacities can be obtained at cryogenic temperature and higher pressure. Further investigations on modified carbon nanostructures may be useful to achieve the target of 7.5 wt.% for automobile applications.
3. Theoretical studies show a strong structural dependence of carbon materials on hydrogen adsorption capacity, especially in CNTs. The defects influence the adsorption capacity.
4. Several theoretical studies predicted amazing storage capacities but were not confirmed experimentally. Also, higher storage capacities like 20 wt.% for metal doped MWCNT and 10 wt.% for CNF measured experimentally are reported in the literature but are to be confirmed.
5. Experimental and theoretical studies on adsorption storage reactors are scarce in the literature. Studies on the design, material, and thermophysical properties of reactors can be done for isotherm measurements, especially for automotive applications. These vital issues will be a good technical contribution in the field of hydrogen-adsorption systems for onboard applications.

Spill-over is one of the phenomena invoked by the transport of hydrogen from the site of impact to other normally inactive sites. This phenomenon has been investigated and is commonly accepted alternate way of surface transport. This transport requires a transporting medium and in the case of hydrogen, it is usually water and its fragments. In the case of carbon, this transporting medium can be either adsorbed water species or the carbon species themselves. The role of spillover in hydrogen sorption and storage needs more information.

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