

THERMODYNAMIC CHARACTERISTICS AND ATOMIC MECHANISMS OF HYDROGENATION-DEHYDROGENATION OF GRAPHENE STRUCTURES

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Abstract. The results of the study (by methods of thermodynamic analysis of a number of the most cited experimental and theoretical data) characteristics of the thermal stability of hydrogenated membrane and epitaxial graphenes, as well as the atomic mechanisms of the processes of hydrogenation and dehydrogenation, are presented. A discrepancy of some theoretical data for graphene with the results of thermodynamic "verification" is shown. It is considered the rate-limiting stages and atomic mechanisms of processes of atomic hydrogen chemisorption with membrane and epitaxial graphenes, relevance to the problem of the efficient and safety storage of hydrogen in the fuel cell powered ecological vehicles.

Keywords: free-standing graphene membranes, graphanes, epitaxial graphenes, hydrogenation and dehydrogenation, the atomic mechanisms, the thermal stability characteristics, the hydrogen on-board storage problem

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CONTENTS

1. INTRODUCTION (145)
 2. THE STUDY RESULTS (146)
 3. CONCLUSIONS (146)
- REFERENCES (147)

1. INTRODUCTION

As noted in a number of articles 2007 through 2014, hydrogenation of graphene-layers-systems, as a prototype of covalent chemical functionality and an effective tool to open the band gap of graphene, is of both fundamental and applied importance (Geim and Novoselov, 2007; Palerno, 2013).

It is relevant to the current problems of thermodynamic stability and thermodynamic characteristics of the hydrogenated graphene-layers-systems (Sofa et al., 2007; Openov and Podlivaev, 2010; Han et al., 2012), and also to the current problem of hydrogen on-board storage (Akiba, 2011; Zuettel, 2011; DOE targets, 2012).

The results of Nechaev (2010), and also Table 1A and B in the present paper, of thermodynamic analysis of a number of experimental data point that some specific local sp³-like hybridization, without

the diamond-like strong distortion of the graphene network, may be manifested itself in the cases of hydrogen atoms dissolved between graphene layers in isotropic graphite, graphite nanofibers (GNFs) and nanostructured graphite, where obviously there is a situation similar (in a definite degree) to one of the rigidly fixed graphene membranes. As far as we know, it has not been taken into account in many recent theoretical studies.

In this connection, it is expedient to note that there are a number of theoretical works showing that hydrogen chemisorption corrugates the graphene sheet in fullerene, carbon nanotubes, graphite and graphene, and transforms them from a semimetal into a semiconductor (Sofa et al., 2007; Elias et al., 2009). This can even induce magnetic moments (Yazyev and Helm, 2007; Lehtinen et al., 2004; Boukhvalov et al., 2008). Previous theoretical studies suggest that single-side hydrogenation of ideal graphene would be thermodynamically unstable (Boukhvalov et al., 2008; Zhou et al., 2009). Thus, it remains a puzzle why the single-side hydrogenation of epitaxial graphenes is possible and even reversible,

and why the hydrogenated species are stable at room temperatures (Elias et al., 2009; Sessi et al., 2009). This puzzling situation is also considered in the present analytical study. Xiang et al. (2010) noted that their test calculations show that the barrier for the penetration of a hydrogen atom through the six-member ring of graphene is larger than 2.0 eV. Thus, they believe that it is almost impossible for a hydrogen atom to pass through the six-member ring of graphene at room temperature (from a private communication with Xiang et al. (2009).

In the present analytical study, a real possibility of the penetration is considered when a hydrogen atom can pass through the graphene network at room temperature. This is the case of existing relevant defects in graphene, that is, grain boundaries, their triple junctions (nodes) and/or vacancies (Brito et al., 2011; Zhang et al., 2014; Banhart et al., 2011; Yazyev and Louie, 2010; Kim et al., 2011; Koepke et al., 2013; Zhang and Zhao, 2013; Yakobson and Ding, 2011; Cockayne et al., 2011; Zhang et al., 2012; Eckmann et al., 2012). The present study is related to revealing the atomic mechanisms of reversible hydrogenation of epitaxial graphenes, compared with membrane graphenes. It is related

to a further development and modification of our previous analytical results (2010-2014), particularly published in the open access journals. Therefore, in the present paper, the related figures 1-25 from our “open” publication (Nechaev and Veziroglu, 2013) are referred.

2. THE STUDY RESULTS

In the next parts of this paper, results of thermodynamic analysis, comparison and interpretation of some theoretical and experimental data are presented (in **Tables 1-3**), which are related to better understanding and/or solving of the open questions mentioned above.

3. CONCLUSIONS

(1) The chemisorption processes in the free-standing graphene membranes are related to a non-diffusion-rate-limiting case. They can be described and interpreted within the physical model of the Polanyi-Wigner equation for the first order rate reactions, but not for the second order rate reactions.

The desorption activation energy is of $\Delta H_{\text{des. (membr.)}} = \Delta H_{\text{C-H (membr.)}} = 2.6 \pm 0.1$ eV. It coincides (within the errors), in accordance with the Polanyi-Wigner

Table 1A

Theoretical, experimental and analytical values of some related quantities

Material	Value/Quantity				
	$\Delta H_{\text{(C-H)}}^*$ (eV)	$\Delta H_{\text{(bind.)}}^*$ eV	$\Delta H_{\text{(C-C)}}^*$ (eV)	$\frac{\Delta H_{\text{(des.)}}^*}{\Delta H_{\text{(ads.)}}^*}$ (eV)	$K_{0(\text{des.})}^* \text{ s}^{-1}$ ($L \approx (D_{\text{app}} / K_{0(\text{des.})}^*)^{1/2}$)
Graphane CH (Sofa et al., 2007)	2.5 ± 0.1 (analysis)	6.56 (theory)	2.7 (analysis)		
Graphane CH (Dzhurakhalov and Peeters, 2011)	1.50 (theory)	5.03 (theory)	2.35 (analysis)		
Graphane CH (Openov and Podlivaev, 2010)	2.46 ± 0.17 (analysis)			2.46 ± 0.17 (theory)	2.0×10^{15} (analysis)
Free-standing graphene-like membrane (Elias et al., 2009)	There are no experimental values in the work			if 2.5 ± 0.1	then 7×10^{12}
				if 2.6 ± 0.1	then 5×10^{13}
				(1.0 ± 0.2) (analysis)	$K_{0(\text{ads.})}^* \approx K_{0(\text{des.})}^*$
				then 1.84	if 7×10^{12}
				then 1.94	if 5×10^{13}
				if 0.3	then 0.2
Hydrogenated epitaxial graphene (Elias et al., 2009)	There are no experimental values in the work			if 0.6	then 80
				if 0.9	then 3.5×10^4
				(0.3 ± 0.2) (analysis)	$(K_{0(\text{ads.})}^* \approx K_{0(\text{des.})}^*) (L \sim d_{\text{sample}})$
Hydrogenated epitaxial* graphene, TDS-peak #1 (Elias et al., 2009)				0.6 ± 0.3 (as processes ~ I-II, ~ model "G", Figure 4) (analysis)	2×10^7 (or $2 \times 10^3 - 2 \times 10^{11}$) ($L \sim d_{\text{sample}}$) (analysis)
Hydrogenated epitaxial* graphene, TDS-peak #2 (Elias et al., 2009)				0.6 ± 0.3 (as processes ~ I-II, ~ model "G", Figure 4) (analysis)	1×10^6 (or $4 \times 10^2 - 2 \times 10^9$) ($L \sim d_{\text{sample}}$) (analysis)
Hydrogenated epitaxial* graphene, TDS-peak #3 (Elias et al., 2009)				0.23 ± 0.05 (as process ~ I, ~ models "F", "G", Fig. 4) (analysis)	2.4 (or 0.8-7) ($L \sim d_{\text{sample}}$) (analysis)
Rigidly fixed hydrogenated graphene membrane (Elias et al., 2009)	There are no experimental values in the work			There are no experimental values in the work	There are no experimental values in the work
Graphene (Dzhurakhalov and Peeters, 2011)		7.40 (theory)	4.93 (analysis)		
Graphite (Nechaev and Veziroglu, 2013)		7.41 ± 0.05 (analysis)	4.94 ± 0.03 (analysis)		
Diamond (Nechaev and Veziroglu, 2013)		7.38 ± 0.04 (analysis)	3.69 ± 0.02 (analysis)		

Table 1B

Theoretical, experimental and analytical values of some related quantities

Material	Value/Quantity			
	$\Delta H_{(C-H)}$, eV	$\Delta H_{(C-C)}$, eV	$\Delta H_{(des.)}$, eV	$K_{0(des.)}$, s ⁻¹
Hydrofullerene C ₆₀ H ₃₆ (Pimenova et al., 2002)	2.64 ± 0.01 (experiment)			
Hydrogenated carbon nanotubes C ₂ H (Bauschlicher and So, 2002)	2.5 ± 0.2 (theory)			
Hydrogenated isotropic graphite, graphite nanofibers and nanostructured graphite (Nechaev, 2010)	2.50 ± 0.03 (analysis, process III, model "F*")	4.94 ± 0.03 (analysis)	2.6 ± 0.03 (analysis, process III)	There are empirical values in the work (analysis of experiment)
Hydrogenated isotropic graphite, graphite nanofibers, nanostructured graphite, defected carbon nanotubes (Nechaev, 2010)	2.90 ± 0.05 [analysis, process II, models "H", "G" (Figure 4)]		1.24 ± 0.03 (analysis, process II)	There are empirical values in the work (analysis of experiment)
Hydrogenated isotropic graphite, carbon nanotubes (Nechaev, 2010)	2.40 ± 0.05 [analysis, process I, models "F", "G" (Figure 4)]		0.21 ± 0.02 (analysis, process I)	There are empirical values in the work (analysis of experiment)
Hydrogenated isotropic and pyrolytic and nanostructured graphite (Nechaev, 2010)	3.77 ± 0.05 [analysis, process IV, models "C", "D" (Figure 4)]		3.8 ± 0.5 (analysis, process IV)	There are empirical values in the work (analysis of experiment)

model, with the values of the similar quantities for theoretical graphanes (Table 1A) possessing of a diamond-like distortion of the graphene network. It also coincides (within the errors) with the value of the similar quantity [process III, model "F*" (Table 1B)] manifested in graphitic structures and nanostructures, not possessing of a diamond-like distortion of the graphene network (an open theoretical question).

The desorption frequency factor is of $K_{0(des.(membr.))} = \nu_{C-H(membr.)} \approx 5 \times 10^{13} s^{-1}$ (Table 1A). It is related to the corresponding vibration frequency for the C-H

bonds (in accordance with the Polanyi-Wigner model).

The adsorption activation energy (in the approximation of $K_{0ads.} \approx K_{0des.}$) is of $\Delta H_{ads.(membr.)} = 1.0 \pm 0.2$ eV (Table 1A). The heat of adsorption of atomic hydrogen by the free standing graphene membranes (Elias et al., 2009) may be as $(\Delta H_{ads.(membr.)} - \Delta H_{des.(membr.)}) = -1.5 \pm 0.2$ eV (an exothermic reaction).

(2) The hydrogen chemisorption processes in epitaxial graphenes (Tables 1A, 2 and 3), unlike

Table 2

Analytical values of some related quantities

Material	Value/Quantity		
	$\frac{\Delta H_{(des.)}}{\{\Delta H_{(ads.)}\}}$, eV	$K_{0(des.)}$, s ⁻¹ { $L \approx (D_{0app.III} / K_{0(des.)})^{1/2}$ }	$\tau_{0.63(des.)553K}$, s { $\tau_{0.63(ads.)300K}$, s}
Graphene flakes/SiO ₂ (Wojtaszek et al., 2011)	0.11 ± 0.07 (as process ~ I, ~ models "F", "G", Fig. 4) {0.1 ± 0.1}	0.15 (for 0.11 eV) { $L \sim d_{sample}$ }	0.7 × 10 ² {0.9 × 10 ³ }
Graphene/Ni HOPG (Castellanos-Gomez et al., 2012)			1.3 × 10 ² - 2.6 × 10 ² {0.5 × 10 ³ - 1.0 × 10 ³ }
SiC-D/QFMLG-H (Bocquet et al., 2012)	0.7 ± 0.2 (as processes ~ I - II, ~ model "G", Figure 4)	9 × 10 ² (for 0.7 eV) { $L \sim d_{sample}$ }	2.7 × 10 ³
SiC-D/QFMLG (Bocquet et al., 2012)	2.0 ± 0.6 (as process ~ III, ~ model "F*")	1 × 10 ⁶ (for 2.0 eV) 6 × 10 ⁸ (for 2.6 eV) { $L \approx 22$ nm}	1.7 × 10 ¹² 8 × 10 ¹⁴
Graphene/SiO ₂ (Elias et al., 2009) (Table 1A)	if 0.3 if 0.6 if 0.9 (as processes ~ I-II, ~ model "G", Figure 4) {0.3 ± 0.2}	then 0.2 then 0.8 × 10 ² then 3.5 × 10 ⁴ { $L \sim d_{sample}$ }	0.3 × 10 ² 3.7 × 10 ³ 4.6 × 10 ³ {2.5 × 10 ³ }
Graphene*/SiO ₂ (TDS-peak #3) (Elias et al., 2009) (Table 1A)	0.23 ± 0.05 (as process ~ I, ~ models "F", "G", Figure 4)	2.4 (for 0.23 eV) { $L \sim d_{sample}$ }	0.5 × 10 ²
Graphene*/SiO ₂ (TDS-peak #2) (Elias et al., 2009) (Table 1A)	0.6 ± 0.3 (as processes ~ I - II, ~ model "G", Figure 4)	1 × 10 ⁶ (for 0.6 eV) { $L \sim d_{sample}$ }	0.3
Graphene*/SiO ₂ (TDS-peak #1) (Elias et al., 2009) (Table 1A)	0.6 ± 0.3 (as processes ~ I - II, ~ model "G", Figure 4)	2 × 10 ⁷ (for 0.6 eV) { $L \sim d_{sample}$ }	1.5 × 10 ⁻²

ones for the free-standing graphene membranes (Table 1A), are related to a diffusion-rate-limiting case. They can be described and interpreted within the known diffusion approximation of the first order rate reactions, but not within the physical models of the Polanyi-Wigner equations for the first or for the second order rate reactions.

The desorption activation energy is of $\Delta H_{\text{des.}} = 0.5 \pm 0.4$ eV. The quantity of $\ln K_{0\text{des.}}^{\text{(epitax.)}}$ is of 5 ± 8 , and the per-exponential factor of the desorption rate constant is of $K_{0\text{des.}}^{\text{(epitax.)}} \approx 1.5 \times 10^2 \text{ s}^{-1}$ (or $5 \times 10^{-2} - 5 \times 10^5 \text{ s}^{-1}$). The adsorption activation energy (in a rough approximation of $K_{0\text{ads.}} \approx K_{0\text{des.}}$) is of $\Delta H_{\text{ads.}}^{\text{(epitax.)}} = 0.3 \pm 0.2$ eV.

The above obtained values of characteristics of dehydrogenation of the epitaxial graphenes can be presented as $\Delta H_{\text{des.}} \sim Q_{\text{app.I}}$ and $K_{0\text{des.}} \sim (D_{0\text{app.I}}/L^2)$, where $Q_{\text{app.I}}$ and $D_{0\text{app.I}}$ are the characteristics of process I (Table 1B), $L \sim d_{\text{sample}}$, that is, being of the order of diameter (d_{sample}) of the epitaxial graphene samples. The diffusion-rate-limiting process I is related to the chemisorption models “F” and “G” (Fig. 4 [8]). These results unambiguously point that in the epitaxial graphenes the dehydrogenation processes are rate-limiting by diffusion of hydrogen, mainly, from chemisorption “centers” [of “F” and/or “G” types (Fig. 4)] localized on the internal graphene surfaces to the frontier edges of the samples. These results also point that the solution and the diffusion of molecular hydrogen occurs in the interfaces between the graphene layers and the substrates. It differs from the case of the graphene neighbor

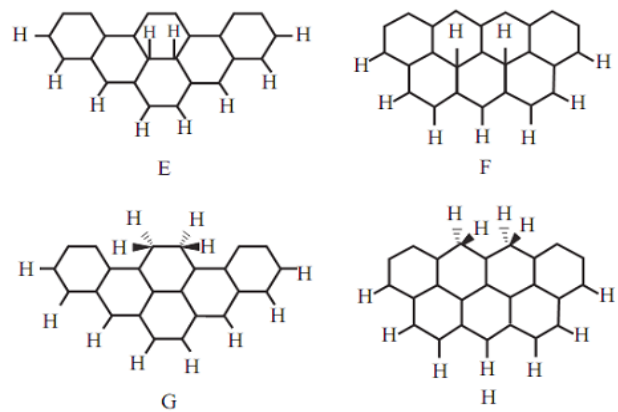


Fig. 4 [8]. Some theoretical models (*ab initio* molecular orbital calculations) chemisorption of atomic hydrogen on the basal and edge planes of graphite [Yang and Yang, 2002].

layers in graphitic structures and nanostructures, where only atomic hydrogen solution and diffusion can occur (process III, model “F*”, Table 1B). Such an interpretation (model) is direct opposite, relevance to the supposition (model) of a number of researchers, those believe in occurrence of hydrogen desorption processes, mainly, from the external epitaxial graphene surfaces. And it is direct opposite to the supposition-model of many scientists that the diffusion of hydrogen along the graphene-substrate interface is negligible.

(3) The possibility, and particularly, the physics of intercalation of a high density molecular hydrogen (up to solid H_2) in closed nanoregions, in hydrogenated *GNFs* have been discussed, in connection to the analytical results (Tables 1 to 3) and the empirical facts considered in this paper.

Table 3

Analytical values of some related quantities

Sample	Values/Quantities			
	$\Delta H_{(\text{des.})1}^{\text{1}}$ (eV)	$K_{0(\text{des.})1}^{\text{1}} \text{ (s}^{-1}) \{L\}$	$\Delta H_{(\text{des.})2}^{\text{2}}$ (eV)	$K_{0(\text{des.})2}^{\text{2}} \text{ (s}^{-1}) \{L\}$
1LG-15W (graphene) (Luo et al., 2009)	0.6 ± 0.2 (as processes ~I-II, ~model “G”, Figure 4)	2×10^4 {L ~ d_{sample} }	0.19 ± 0.07 (as process ~I, ~models “F”, “G”, Figure 4)	3×10^{-2} {L ~ d_{sample} }
2LG-15W (bi-graphene) (Luo et al., 2009)			0.9 ± 0.3 (as processes ~I-II, ~model “G”, Figure 4)	1×10^3 {L ~ d_{sample} }
1LG-5W (graphene) (Luo et al., 2009)	0.15 ± 0.04 (as process ~I, ~ models “F”, “G”, Figure 4)	2×10^{-2} {L ~ d_{sample} }	0.31 ± 0.07 (as process ~ I [14], ~models “F”, “G”, Figure 4)	5×10^{-1} {L ~ d_{sample} }
2LG-5W (bi-graphene) (Luo et al., 2009)	0.50 ± 0.15 (as processes ~I-II, ~model “G”, Figure 4)	2×10^3 {L ~ d_{sample} }	0.40 ± 0.15 (as processes ~ I-II, ~model “G”, Figure 4)	1.0 {L ~ d_{sample} }
HOPG (Hornekaer et al., 2006), TDS-peaks 1, 2	0.6 ± 0.2 (as processes ~ I - II, ~model “G”, Figure 4)	1.5×10^4 {L ~ d_{sample} }	1.0 ± 0.3 (as processes ~ I-II, ~ model “G”, Figure 4)	2×10^6 {L ~ d_{sample} }
Graphene/SiC (Watcharinyanon et al., 2011)			3.6 (as process ~IV [14], ~models “C”, “D”, Figure 4)	$2 \times 10^{14} \sim v_{\text{(C-H)}}$ {L ~ 17nm}
HOPG, TDS-peaks 1, 2	2.4 (Waqar et al., 2000) (as process ~III, ~model “F*”)	2×10^{10} {L ~ 4 nm}	4.1 (Waqar et al., 2000) (as process ~IV, ~models “C”, “D”, Figure 4)	
HOPG, TDS-peak 1 (Waqar et al., 2000)	2.4 ± 0.5 (as process ~ III, ~model “F*”)			

It is relevant for developing of a key breakthrough nanotechnology of the hydrogen on-board efficient and compact storage (Fig. 25 [8]) – the very current problem.

Such a nanotechnology may be developed within a reasonable (for the current hydrogen energy demands and predictions) time frame of several years. International cooperation is necessary.

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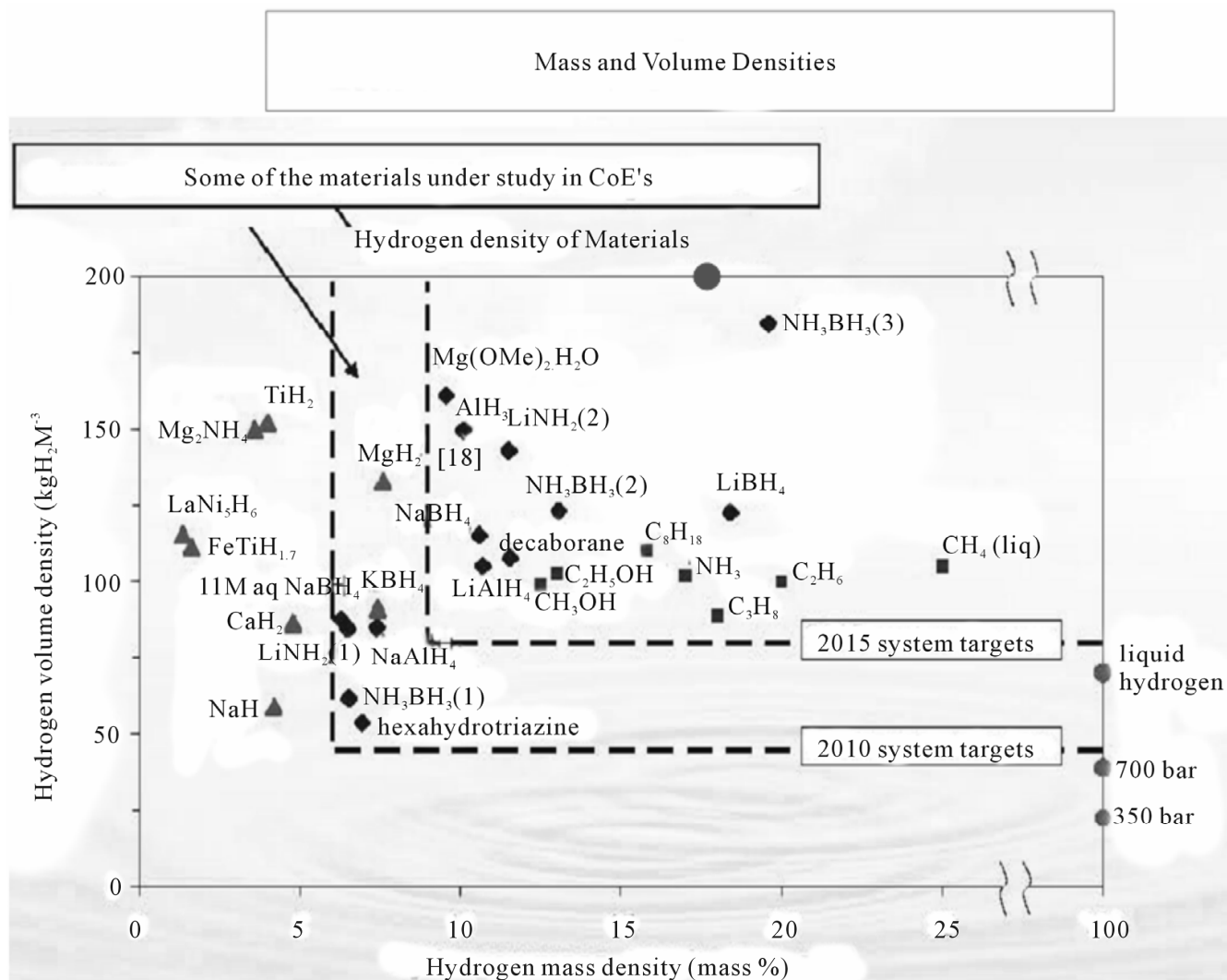


Fig. 25 [8]. It is shown [71] (in the face of known achievements) U.S. DOE targets [74], relevant to gravimetric and volumetric hydrogen on-board storage densities for 2010 (6.0 mass.% H₂, 45 kg(H₂)/m³(systems)) and for 2015 (9.0 mass.% H₂, 81 kg(H₂)/m³(systems)). The additional red circle is related to the solid hydrogen intercalated into the hydrogenated GNFs.

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